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In response to RCRA, EPA issues permits for hazardous waste land treatment facilities. RCRA standards require that the owner or operator of a hazardous waste land treatment facility demonstrate, prior to application of the waste, that hazardous constituents in the waste can be completely degraded, transformed, or immobilized within the treatment zone, and that human health and the environment are protected by the design and operation strategy used for the waste at the site. Successful performance of the land treatment demonstration is required in order to obtain a permit under 40 CFR Parts 264 and 270.

This document was prepared to give the applicant and the regulatory agency guidance on the information necessary to assist in choosing and implementing the land treatment demonstration approach. The technical approach for accomplishing the goal of demonstrating land treatment presented in this manual provides a methodology for both evaluating site, soil, and waste characteristics, and assessing waste treatment processes within the treatment zone soil.

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PREFACE

Subtitle C of the Resource Conservation and Recovery Act (RCRA) requires the U.S. Environmental Protection Agency (U.S. EPA) to establish a federal hazardous waste management program. This program must ensure that hazardous wastes are handled safely from generation to final disposition. The U.S. EPA issued a series of hazardous waste regulations under Subtitle C of RCRA, published in 40 Code of Federal Regulations (CFR) Parts 260 through 265, 270 and 124.

Parts 264 and 265 of 40 CFR contain standards applicable to owners and operators of all facilities that treat, store, or dispose of hazardous wastes. Wastes are identified or listed as hazardous under 40 CFR Part 261. The Part 264 standards are implemented through permits issued by authorized States or the EPA in accordance with 40 CFR Part 124 and Part 270 regulations. Land treatment, storage, and disposal (LTSD) regulations in 40 CFR Part 264 issued on July 26, 1982, establish performance standards for hazardous waste landfills, surface impoundments, land treatment units, and waste piles.

This final manual provides guidance on land treatment demonstrations required under Section 264.272 for all owners/operators of hazardous waste land treatment units. The manual contains specific laboratory and field test methods that may be used to complete the demonstration and describes alternative technical approaches and permitting procedures to accommodate the treatment demonstration. This guidance does not supersede the regulations promulgated under RCRA and published in the Code of Federal Regulations, and is not intended to suggest that other approaches to the demonstration of land treatment might not also satisfy the regulatory standards.

This final guidance manual was prepared based on comments received concerning the December 1984 draft document (EPA/530-SW-84-015), titled Draft Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations: For Public Comment.

EXECUTIVE SUMMARY

Hazardous waste land treatment (HWLT) can be considered as the intimate mixing or dispersion of wastes into the upper zone of a soil system, with the objectives of degradation, transformation, and/or immobilization, leading to an environmentally acceptable assimilation of the waste. The overall goal is the simultaneous ultimate disposal and treatment of hazardous wastes, while ensuring protection of public health and the environment.

The U.S. Environmental Protection Agency (U.S. EPA) issued standards in July 1982, required by the Resource Conservation and Recovery Act (RCRA), that are used for permitting a hazardous waste land treatment (HWLT) facility. The regulations define the principal elements of a HWLT program as: a) the wastes to be applied, b) the design and operating measures necessary to maximize degradation, transformation, and immobilization of the hazardous waste constituents, and c) an unsaturated zone monitoring program.

A land treatment demonstration (LTD) addresses the requirement in the regulations that the owner or operator of a land treatment unit must demonstrate, prior to application of the waste, that hazardous constituents in the waste can be completely degraded, transformed, or immobilized in the treatment zone. An LTD is also required to establish the protectiveness of human health and the environment for the design and management strategy used for a waste at a site.

Successful performance of the land treatment demonstration (LTD) is required in order to obtain a final permit under 40 CFR Parts 264 and 270 for a hazardous waste land treatment unit. In consideration of the complexity of the demonstration requirements, this document was prepared to give the applicant and regulatory agency guidance on the information needed to assist in choosing and implementing the LTD approach.

Permit options for land treatment differ from those of other land disposal technologies. The LTD, much like the trial burn for incinerators, may require a permit to allow for trial performance. A trial performance may be conducted under a short-term demonstration permit or a two-phase permit. It is also possible to apply directly for a full scale permit. The applicable permitting scenario depends in part on 1) whether the unit is new or existing, 2) the conditions of the site, and 3) past, present, and planned operations.

The technical approach to accomplishing the goal of demonstrating land treatment is to provide a methodology for evaluating site, soil, and waste characteristics and for assessing waste treatment processes within the treatment zone soil. The methodology is used to determine the potential for a soil to assimilate a candidate hazardous waste (soil site assimilative capacity; SSAC) so that there is no statistically significant release to the environment from the treatment zone.

While much of the information preliminary to the LTD should have been supplied as part of other permit application requirements, this document provides supplementary guidance on some aspects of these application requirements. Of particular importance for existing units (ISS) is guidance on a reconnaissance survey of soil and hazardous constituent sampling and analysis. Data from this investigation are used to define the spatial distribution of hazardous constituents across HWLT units and to formulate the permit and treatment demonstration approach.

The logic and flow of information for making decisions in choosing the permit approach and the technical elements in the LTD involve answering a series of questions. The questions ask 1) whether the unit is new or existing, 2) whether hazardous constituent data have been collected along with other Part B information, 3) whether the unit is operating effectively to treat wastes, 4) whether past activities can be adequately documented from literature, past records, and operating data, and 5) whether major design and operation changes are planned. The answers to these questions, and the judgment of the regulatory agency, determine which of the LTD scenarios will be employed.

Technical methods for performing each step of the LTD are presented in this manual. Methods discussed include reconnaissance surveys, laboratory analyses, mathematical modeling, and field plot studies. These methods are not necessarily listed in order of performance nor are they all required in any given case. A technical approach section discusses issues common to all methods, such as statistical and analytical aspects of an LTD.

Volatilization will not be directly measured in the LTD methodology presented in this guidance manual. The Office of Air Quality Programs and Standards (OAQPS), U.S. EPA, is currently developing air emission rules for all RCRA facilities. Also, the Robert S. Kerr Environmental Research Laboratory (RSKERL), U.S. EPA, is currently evaluating methodologies for assessing volatilization specifically for land treatment facilities. However, to impose guidelines or requirements at the present time is considered premature and may be confusing, since no standard methods are currently available for measuring volatile emissions. Where obvious air emission problems are identified on a case-by-case basis, permit writers may address volatilization under the omnibus provision of HSWA Section 3005(c)(3).

A mathematical model based on the model developed by the U.S. EPA (RSKERL) for use in banning specific hazardous wastes from land treatment is presented in this guidance manual for integrating the treatment processes of biodegradation and immobilization. A mathematical description of the land treatment system provides a unifying framework for the evaluation of laboratory screening and field data. Specifically, the model provides a framework for determining the effects of (1) design and operating parameters (loading rate, loading frequency, irrigation, amendments to increase degradation; (2) site characteristics (soil type, soil horizons, soil permeability); and (3) environmental parameters (season, precipitation) on treatment performance. Also, the model can be used for comparison of the effectiveness of treatment using different design and operating practices in order to maximize treatment, and for the selection of principal hazardous constituents for monitoring waste performance.

Results of field analysis, where field studies are selected based on a laboratory assessment using the model, will be useful for verification of the model and for providing information for modifying the model. Also where site, soil, and degradation kinetic information can be developed based on field sampling, minimal laboratory analyses are required (determination of partition coefficients) for using the model.

CONTENTS

Acknowledgments ii
Preface iii
Executive Summary iv
Figures x
Tables xi

1 Introduction and Administrative Approach to the Performance of a land treatment demonstration 1
  1.1 Introduction 1
  1.2 Basic LTD Concepts 2
    1.2.1 Toxicity of the waste to the soil treatment medium 2
    1.2.2 Degradation of hazardous constituents 4
    1.2.3 Transformation/detoxification of hazardous constituents 4
    1.2.4 Immobilization of hazardous constituents . . . 4
  1.3 Regulatory Requirements 5
  1.4 Administration Options for Land Treatment Demonstrations 10
  1.5 Criteria for Choosing a Land Treatment Demonstration Scenario 15
  1.6 Implications of the Hazardous and Solid Waste Amendments of 1984 (HSWA) for Land Treatment Demonstrations and Facilities 24
2 Technical Approach to the Performance of an LTD 26
  2.1 Evaluation of Treatment Process 26
  2.2 Determination of the Site/Soil Assimilative Capacity (SSAC) for a Candidate Waste 29
    2.2.1 The toxicity component of the SSAC 29
    2.2.2 The immobilization component of the SSAC . . . 30
    2.2.3 The biodegradation component of the SSAC . . . 31
    2.2.4 The transformation/detoxification component of the SSAC 31
    2.2.5 Calculation of the SSAC 32
    2.2.6 Principal hazardous constituents (PHCs) 32
    2.2.7 Use of the SSAC for design and management . . . 32
  2.3 Design and Management Parameters 33
    2.3.1 Loading rate 33
    2.3.2 Waste application frequency 34
    2.3.3 Waste application method 34
    2.3.4 Operation and management factors 34
    2.3.5 Evaluation of the effect of design and management parameters on SSAC values 35
  2.4 Field Verification Study 35

CONTENTS (CONTINUED)

2.5 Analytical Aspects of Conducting an LTD 36
2.6 Analytical Costs 43
3 Procedures for Collecting Field Information for Reconnaissance Survey and Field Verification Studies 45
3.1 Introduction 45
3.2 Waste Characterization 46
3.2.1 Sampling and sample collection 47
3.2.2 Sample handling and storage 48
3.2.3 Analysis of waste characteristics 48
3.3 Waste Management Records for an Existing Site 49
3.4 Soil Characterization 49
3.4.1 Soil survey 49
3.4.2 Characterization of distribution of hazardous constituents in soil (existing sites only) . . . 53
3.5 Groundwater Monitoring 57
3.6 Data Interpretation and Presentation 59
4 Predictive Tool for Land Treatment Demonstrations 61
4.1 Introduction 61
4.2 Model Description 62
4.2.1 Definition of terms 62
4.2.2 Model construct 63
4.2.3 Immobilization/transport 63
4.2.4 Constituent degradation 66
4.2.5 Input 66
4.2.6 Output 66
4.3 Model Application 69
4.4 Examples 70
5 Laboratory Analyses and Studies for Selecting Design and Operation Conditions 74
5.1 Introduction 74
5.2 Waste Characterization 74
5.3 Soil Characterization 75
5.4 Toxicity of Waste to the Soil Treatment Medium 75
5.4.1 Possible assays 75
5.4.2 Preparation of waste soil mixtures for bioassays 85
5.4.3 Determination of loading rates 86
5.4.4 Data interpretation 88
5.5 Transformation/Detoxification of the Waste:Soil Moisture 89
5.6 Immobilization of Waste Constituents in the Soil Treatment Medium 90
5.6.1 Experimental apparatus for determination of partitioning between oil phase and aqueous phase (Ko) 92
5.6.2 Experimental procedure for determination of Ko. . 94
5.6.3 Experimental apparatus for determination of partitioning between soil phase and aqueous phase (Kd) 95
5.6.4 Experimental procedure for determination of Kd. . 95

CONTENTS (CONTINUED)

5.6.5 Partitioning between aqueous phase and air phase (Kh) 96
5.6.6 Experimental procedure for determination of Kh. . . 96
5.6.7 Three phase partitioning method for Ko and Kh determination 97
5.6.8 Experimental procedure for the combined contamination of Ko and Kh 97
5.6.9 Data handling 99
5.7 Degradation of Waste Constituents in the Soil Treatment Medium 99
5.7.1 Hazardous constituent reduction evaluation techniques 99
6 Monitoring Treatment Performance in the Field 108
6.1 Purpose of Field Verification Study for New and ISS Facilities 108
6.2 Field Verification Study Alternatives 109
6.3 Selection of Design and Management Parameters 110
6.4 Analytical Aspects of Field Verification 111
6.5 Plot Preparation 111
6.6 Waste Application 113
6.7 Field Verification Study Monitoring 113
6.7.1 Collection and analysis for soil core and soil pore liquid samplers 114
6.7.2 Groundwater monitoring 118
6.7.3 Data interpretation 118
7 Quality Assurance Program for Conducting an LTD 119

References 122

Appendices

A Summary of Treatment Demonstration Permit Application Information Requirements 131
B Statistical Considerations for the Performance of an LTD . . . 138
C Information Concerning the HWLT Mathematical Model 147
D Target Detection Limits in Water for Constituents of Petroleum Refining Wastes 169
E Target Detection Limits for Selected Organic Compounds in Water 171
F Extended Ritz Model Fortran Listing 175
G Example of a Monitoring Schedule for a Field Plot Demonstration 198

FIGURES

Number		Page
1.1	Treatment processes and monitoring techniques for a land treatment unit	3
1.2	LTD guidance for selection of appropriate scenario	16
1.3	Specific guidance and information requirements for LTD meeting the definition for Scenario 2	22
1.4	Specific guidance and information requirements for LTD meeting of the definition for Scenario 3	23
4.1	Conceptual description of land treatment system used in extended RITZ model formulation	64
4.2	Transport and partitioning relationships within soil control volumes used in modified RITZ model	65
4.3	Sample constituent total soil concentration profile at selected time periods after initial waste application	68
4.4	Time distributions of naphthalene concentration in the plow zone and depth distributions at specific times in the lower treatment zone	73
5.1	Sample preparation and analysis scheme for the determination of Kh, Kd, and Ko	93
5.2	Apparatus for three-phase partitioning coefficient determinations	98
5.3	Laboratory flask apparatus used for mass balance measurements	101
5.4	Laboratory microcosm apparatus used in laboratory AERR model validation studies	106
C2.1	Sample input data file	153
C2.2	Sample output file	156
C2.3	Sample supplementary output file for graphic displays	162
C3.1	Enhanced RITZ model structure	164

TABLES

Table Page

1.1 Summary of Specific Part B Information Requirements for Land Treatment Facilities 6

1.2 Standards Given in 40 CFR Section 264.272 - Treatment Demonstration 8

1.3 Standards Given in 40 CFR Section 264.271 Related to Section 264.272 - Treatment Program 8

1.4 Standards Given in 40 CFR Section 264.273 Related to Part 264.272 - Design and Operating Requirements 9

1.5 Land Treatment Permit Elements 11

1.6 Permit Application Content for Each Permit Element 12

1.7 Information Required to Assess Planned Changes in Design and Operation and to Assess the Suitability of the Use of Scenario 2 20

2.1 Monitoring and Evaluation Strategies to Assess Treatment Processes in a Land Treatment Demonstration 27

2.2 Design and Operation Parameters for LTDs 29

2.3 Suggested Analytical Information for an LTD 37

2.4 Summary of Suggested Maximum Metal Accumulations Where Materials Will be Left in Place at Closure 42

2.5 Suggested Metal Loadings for Metals with Less Well-Defined Information 43

2.6 Estimates of Analytical Costs for Type I, II, and III Analyses. 44

3.1 Useful Waste Management Data and Records 50

3.2 Soil Physical and Chemical Properties To Be Determined in Soil Survey 52

TABLES (CONTINUED)

Table		Page
3.3	Suggested Uses of Field Information	60
4.1	Design/Operational Variables Required for Use in the Extended RITZ Model	67
4.2	Variables Required from Laboratory Analyses, Prediction Methods, Etc., for Use in the Extended RITZ Model	67
4.3	Physical Properties of the Soil Columns Used for Examples 1 Through 4	70
4.4	Operating Parameters and Waste Characteristics for Examples 1 Through 4	71
4.5	Summary of Results for Sample Runs	73
5.1	Toxicity Screening Bioassays Useful in Evaluating Hazardous Waste Applications to Soil	76
6.1	Comparison of Field Verification Alternatives	110
B.1	Frequency Distribution of Soil Properties	140
B.2	Examples of Number of Samples Required to Achieve a Specified Analytical Precision and Level of Confidence, Based on Expected Variability of Sample Concentrations, as Determined in an Exploratory Study	144
D.1	Constituents of Petroleum Refining Wastes	169
E.1	Target Detection Limits for Organic Compounds	171
G.1	Example of a Monitoring Schedule for a Field Plot Study	200

CHAPTER 1

INTRODUCTION AND ADMINISTRATIVE APPROACH TO THE PERFORMANCE OF A LAND TREATMENT DEMONSTRATION

1.1 INTRODUCTION

Under the authority of Subtitle C of the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (U.S. EPA) promulgated regulations for the treatment, storage, and disposal of hazardous waste in land treatment units (40 CFR Part 264). These regulations require a permit for the operation of a hazardous waste land treatment (HWLT) unit. Section 264.272 stipulates that the first step in obtaining such a permit is to complete a land treatment demonstration (LTD).

The land treatment demonstration is used by the permitting authority to define two elements of the land treatment program. First, the demonstration establishes what wastes may be managed at the unit. Wastes that will be applied must be subject to degradation, transformation, and/or immobilization processes in the soil such that hazardous constituents are not expected to migrate from the defined treatment zone. Second, results of the treatment demonstration will be used to define the initial set of waste management practices, including loading rates, that will be incorporated into the facility permit.

The treatment demonstration can be completed using information derived from published literature, laboratory studies, field studies, and/or actual facility operating experience. However, the U.S. EPA generally believes that an inadequate data base exists in the published literature at the present time to predict unit-specific waste-soil interactions. Consequently, most land treatment permit applicants must use laboratory studies, field studies, actual facility operating experience, or a combination of these approaches to complete the treatment demonstration.

One criterion for whether an LTD permit is needed is if field or laboratory data will be collected. The regulations assume that any form of disposal, even in a small-scale laboratory situation, requires a permit.

The purpose of this manual is to provide guidance on specific approaches, including laboratory and field test methods, that may be used to complete the treatment demonstration as required under Section 264.272 for owners and operators of hazardous waste land treatment units. The manual addresses policy and technical aspects of the demonstration, and describes alternative permitting approaches.

This manual expands the general guidance on treatment demonstrations already provided in the following documents:

- Permit Applicants' Guidance Manual for Hazardous Waste Land Treatment, Storage, and Disposal Facilities (U.S. EPA, 1984a);
- RCRA Guidance Document: Land Treatment Units (U.S. EPA, 1983b).

The U.S. EPA wishes to emphasize that the methods described in this manual are for guidance only and are not regulations. An applicant may use alternative methods, provided that these methods comply with the applicable regulatory requirements. EPA believes that methods which are equivalent to or more comprehensive than those described herein will meet the regulatory requirements. While the U.S. EPA believes that the specifications provided for each of the described test methods are a reasonable estimate for a complete treatment demonstration in compliance with Section 264.272, the permit writer may modify these specifications as necessary.

1.2 BASIC LTD CONCEPTS

The land treatment demonstration is designed to evaluate the principal processes involved in the treatment of hazardous wastes applied to a land treatment unit. These processes include degradation, transformation, and immobilization. Figure 1.1 shows a conceptual diagram for a land treatment demonstration site, illustrating a mass balance approach. Leaching and volatilization are inversely related to the process of immobilization, and are included for the purpose of illustrating a mass balance around the soil treatment zone for each hazardous constituent. For many wastes, only a fraction of the applied material is considered hazardous under the RCRA definition. Emphasis is therefore placed on identifying and evaluating RCRA Appendix VIII compounds (defined as hazardous constituents in the RCRA regulations, 40 CFR 261).

Figure 1.1 also illustrates the principal monitoring techniques for a field verification study as part of a land treatment demonstration--analysis of wastes, soil cores in and below the treatment zone, soil-pore liquid below the treatment zone, and groundwater monitoring where appropriate.

1.2.1 Toxicity of the Waste to the Soil Treatment Medium

The decomposition of hazardous wastes and the detoxification (transformation) of PHCs in the soil depend primarily on the enzymatic activities of soil microorganisms. The evaluation of the impact of hazardous wastes on indigenous soil microbial populations is important, especially for those wastes containing hazardous constituents specifically designed to inhibit biological activity, e.g., wood preserving wastes, pesticide wastes, etc. The toxicity of a waste can be evaluated using one or more short-term bioassay testing procedures. The choice of a particular assay or a battery of assays to be used must be made based on the ability of selected tests to protect a wide range of metabolic capabilities of decomposers and nutrient cycling soil organisms. The purpose in using bioassays is to ensure that the biological pathways for assimilating a hazardous waste are operative.

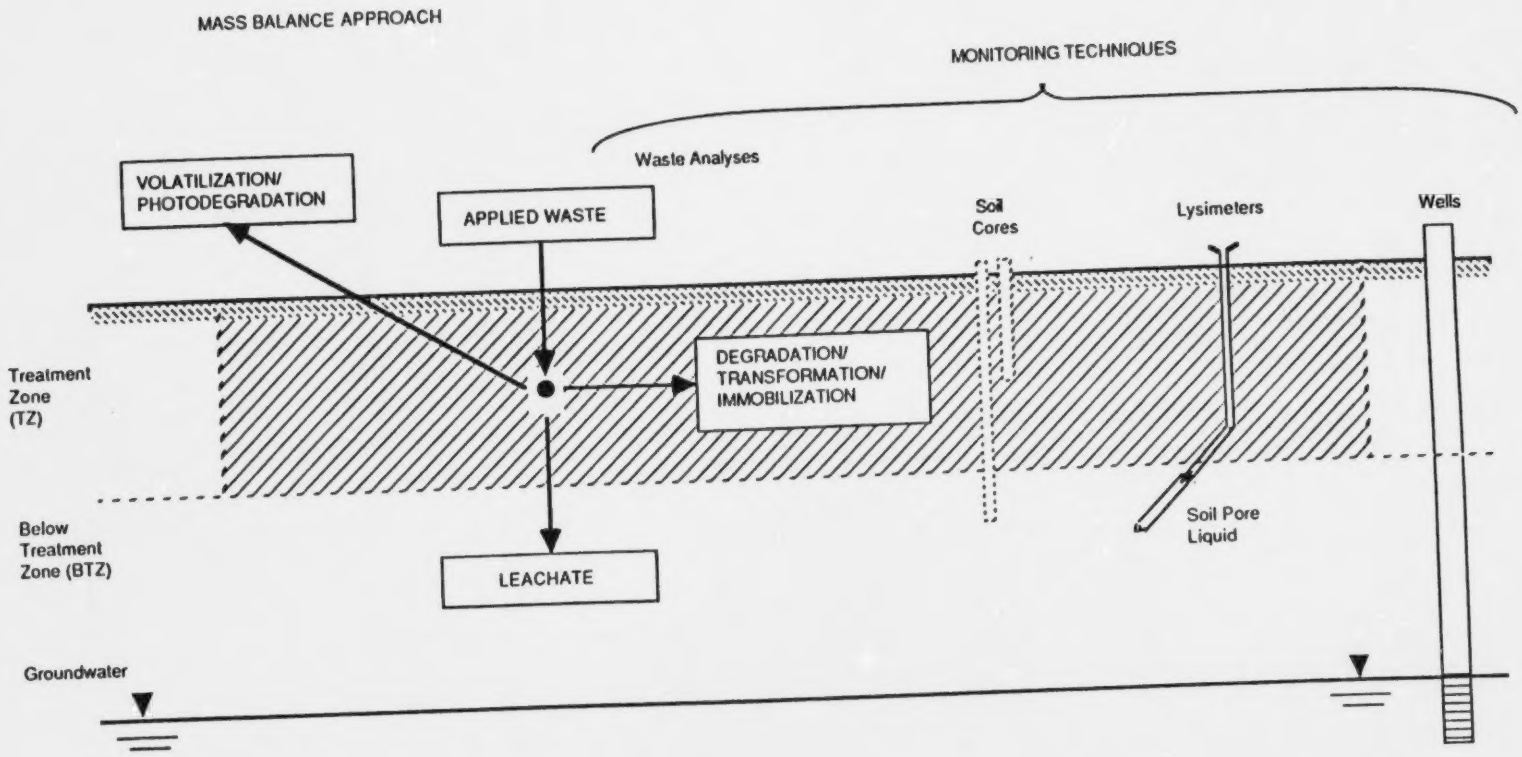
MASS BALANCE APPROACH
MONITORING TECHNIQUES
Waste Analyses
VOLATILIZATION/ PHOTODEGRADATION
APPLIED WASTE
Soil Cores
Lysimeters
Wells
DEGRADATION/ TRANSFORMATION/ IMMOBILIZATION
Treatment Zone (TZ)
Soil Pore Liquid
Below Treatment Zone (BTZ)
LEACHATE
Groundwater

Figure 1.1. Treatment processes and monitoring techniques for a land treatment unit.

Hazardous wastes, applied in too high of a concentration in the soil (loading rate), may reduce the microbial population and/or microbial activity and the concomitant process of biodecomposition. Under these conditions, toxic constituents may leach from the zone of incorporation (ZOI) through the treatment zone and may migrate from the bottom of the treatment zone. Bioassays may be used to help establish waste application rates and frequencies that will not appreciably reduce microbial function in the soil. Bioassays may also be used to follow the transformation (detoxification) of the waste as biodegradation products are formed in the soil, since a candidate waste should not be applied to land unless it is rendered nonhazardous as a result of treatment.

1.2.2 Degradation of Hazardous Constituents

Degradation of waste and waste constituents describes the loss of parent compounds through chemical and biological reactions within the soil/waste matrix. Complete degradation is the term used to describe the process whereby waste constituents are mineralized to inorganic end products, generally including carbon dioxide, water, and inorganic species, such as nitrogen, phosphorus, and sulfur. The rate of degradation may be established by measuring the loss of the parent compound with time.

The biodegradation potential of hazardous constituents in waste(s) to be applied at the proposed land treatment facility is critical as biodegradation usually represents the primary removal mechanism for organic constituents in waste(s). Hazardous constituent degradation rates may be determined from appropriate literature data and/or from experimental procedures described in Chapter 5 of this manual.

1.2.3 Transformation/Detoxification of Hazardous Constituents

The chemical and/or biological conversion of hazardous constituents to less toxic intermediates within the land treatment unit should be evaluated in a determination of hazardous waste land treatability. Transformation may be addressed along with degradation based on parent and intermediate compound characterization procedures. Chemical and bioassay analyses are recommended to ensure that transformation/detoxification processes are active in the soil/waste mixture.

1.2.4 Immobilization of Hazardous Constituents

Immobilization refers to the affinity of a chemical for particulate surfaces in the soil treatment zone. Chemicals that adsorb tightly to soil may be less subject to environmental transport in the solution (leachate) phase and/or in the gaseous (volatile) phase.

Leaching refers to the movement of materials through the treatment zone to deeper soils and/or to groundwater. An LTD for a properly operating land treatment site should show the absence of hazardous constituent migration.

Volatilization refers to the process by which applied materials are lost to the atmosphere. Volatilization will not be directly measured in the LTD methodology presented in this guidance manual. The Office of Air Quality Programs and Standards (OAQPS), U.S. EPA, is currently developing air emission rules for all RCRA facilities. Also, the Robert S. Kerr Environmental Research Laboratory, U.S. EPA, is currently evaluating methodologies for assessing volatilization specifically for land treatment facilities. However, to impose guidelines/requirements at the present time is considered premature and may be confusing since no standard methods are currently available for measuring volatile emissions. Where obvious air emissions are identified on a case-by-case basis, permit writers may address volatilization under the omnibus provision of RCRA.

Subsequent chapters in this manual will explain how these treatment processes are measured and assessed through the use of operating data, reconnaissance surveys, literature information, mathematical modeling, and field plot studies.

1.3 REGULATORY REQUIREMENTS

The approach for land treatment demonstrations (LTDs) is organized to address the hazardous waste land treatment (HWLT) regulations promulgated under the Resource Conservation and Recovery Act, Subtitle C in 40 Code of Federal Regulations (CFR), Section 264.272, titled Treatment Demonstration. The treatment demonstration is conducted in order to obtain a permit to land treat hazardous wastes under the hazardous waste permit program as specified in 40 CFR Part 270. Specifically, 40 CFR Section 270.20 addresses information requirements for a Part B permit for operating a hazardous waste land treatment facility. These information requirements are listed in Table 1.1. The Part B permit information requirements presented in 40 CFR Section 270.20 reflect the standards promulgated in 40 CFR Part 264, and are necessary for EPA to determine compliance with Part 264 standards.

Section 270.20 (a) (3) requires that the Part B permit application for land treatment units outlines a treatment demonstration plan as required under Section 264.272 (Table 1.2). This treatment demonstration plan must include characteristics of the waste(s) to be land treated and a description of the unit that will be simulated in the demonstration, including waste characteristics, treatment zone characteristics, climatic conditions and operating practices. Additional permit requirements of this treatment demonstration plan are presented in detail in the Permit Applicants' Guidance Manual for Hazardous Waste Land Treatment, Storage, and Disposal Facilities (U.S. EPA 1984a) and are summarized in Appendix A of this manual.

A description of a land treatment program to be used at a new or existing facility is specified in Section 270.20(b) as required under Section 264.271 (Table 1.3) and must be submitted with the plans for the treatment demonstration. The land treatment program must be updated as necessary based on results of the completed land treatment demonstration. Table 1.1 indicates general information requirements of the land treatment program including: waste(s) to be land treated, design measures to maximize treatment, procedures for unsaturated zone monitoring, list of hazardous constituents in the

Table 1.1 Summary of Specific Part B Information Requirements for Land Treatment Facilities (40 CFR 270.20)

270.20 (*a). Treatment demonstration plan (as required under 264.272), including:
- (1) Waste and waste characterization
- (2) Data sources to be used in the demonstration
- (3) Laboratory or field tests
  - (i) test type (column leaching, degradation, etc.);
  - (ii) materials and methods, including analytical procedures;
  - (iii) time schedule;
  - (iv) characteristics of the unit that will be simulated in the demonstration (treatment zone, climate, operating practices);

270.20 (b). Land treatment program (as required under 264.271), including:
- *(1) Wastes to be land treated
- *(2) Design measures and operating practices necessary to maximize treatment in accordance with 264.273(a) including:
  - (i) waste application method;
  - (ii) waste application rate;
  - (iii) measures to control soil pH;
  - (iv) enhancement of microbial or enhancement of chemical reactions;
  - (v) control of soil moisture content;
- (3) Procedures for unsaturated zone monitoring including:
  - (i) sampling equipment, procedures, and frequency;
  - (ii) procedures for selecting sampling locations;
  - (iii) analytical procedures;
  - (iv) chain of custody control;
  - (v) procedures for establishing background values;
  - (vi) statistical methods for interpreting results;
  - (vii) justification for any hazardous constituents recommended for selection as principal hazardous constituents (in accordance with criteria for such selection in 264.278(a));
- (4) A list of hazardous constituents reasonably expected to be in, or derived from, the wastes to be land treated based on waste analysis performed pursuant to 264.13
- (5) The proposed dimensions of the treatment zone

270.20 (*c). Design and operation information (as required under 264.273), including:
- (1) Control of run-on
- (2) Collection and control of run-off
- (3) Minimization of run-off of hazardous constituents from the treatment zone
- (4) Management of collection and holding facilities associated with run-on and run-off control systems
- (5) Periodic inspection of the unit (270.14(b)(5))
- (6) Control of wind dispersal of particulate matter, if applicable

Table 1.1. Continued

270.20 (d). Food-chain crops considerations (264.276(a)) (if grown in/on treatment zone)
  (1) Crop characterization
  (2) Characteristics of waste, treatment zone, and waste application method and rate
  (3) Procedures for crop growth, sample collection and analysis and data evaluation
  (4) Characteristics of comparison crop

270.20 (e). Food-chain crops and cadmium considerations (264.276(b))

270.20 (f). Closure considerations, including vegetative cover (refer to 264.28(a)(8), 264.280(c)(2), and 270.14(b)(13))

270.20 (g). Ignitable or reactive waste considerations (requirements in 264.281)

270.20 (h). Incompatible wastes and materials considerations (requirements in 264.282)

⌊48 FR 14228, April, 1983
48 FR 30114, June 30, 1983⌋

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*Information developed in or related specifically to Section 264.272.

Table 1.2 Standards Given in 40 CFR Section 264.272 - Treatment Demonstration

264.272 (a). Hazardous constitutents in a waste to be land treated must be demonstrated to be completely degraded, transformed, or immobilized in the treatment zone

264.272 (b). Information sources for LTD include:
(1) Field tests
(2) Laboratory analyses
(3) Available data
(4) Operating data from existing units

264.272 (c). Requirements when using field test and laboratory analyses
(1) Simulate characteristics and operating conditions for proposed unit including
  (i) characteristics of the waste;
  (ii) climate in the area;
  (iii) topography of the surrounding area;
  (iv) characteristics of the soil in the treatment zone (including depth);
  (v) operating practices to be used at the unit;
(2) Show that hazardous constituents in the waste will be completely degraded, transformed, or immobilized in the treatment zone
(3) Conducted in a manner that protects human health and the environment considering:
  (i) characteristics of the waste to be tested;
  (ii) operating and monitoring measures taken during the course of the test;
  (iii) duration of the test;
  (iv) volume of waste used in the test;
  (v) for field tests, the potential for migration of hazardous constituents to groundwater or surface water;

Table 1.3 Standards Given in 40 CFR Section 264.271 Related to Section 264.272 - Treatment Program

264.271 (a). Facility permit specifications include:
(1) Wastes capable of treatment at the unit based on 264.272
(2) Design measures and operating practices necessary to maximize the success of degradation, transformation, and immobilization processes in the treatment zone in accordance with 264.273(a)

264.271 (c)
(2) The maximum depth of the treatment zone may be no more than 5 feet (1.5 m) below the soil surface and no less than 3 feet (1 m) above the seasonal high water table.

waste(s) to be land treated and the proposed dimensions of the treatment zone. Facility design, construction and operation and maintenance information must also be provided to the U.S. EPA as required under Section 264.273 (Table 1.4). The reader is referred to the Permit Applicants' Guidance Manual for Hazardous Waste Land Treatment, Storage and Disposal Facilities U.S. EPA (1984a) Section 7.4, Land Treatment Program, and Section 7.11, Checklist of Permit Application Requirements for Land Treatment Units.

Table 1.4 Standards Given in 40 CFR Section 264.273 Related to Part 264.272 - Design and Operating Requirements

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264.273(a). Maximize treatment

Use conditions established in 264.272 (design and operating conditions used in 264.272) as a basis for facility permit specifications (minimum):

(1) Rate and method of waste application
(2) Measures to control soil pH
(3) Measures to enhance microbial or chemical reactions
(4) Measures to control the moisture content of the treatment zone

264.273(f). If the treatment zone contains particulate matter which may be subject to wind dispersal, the owner or operator must manage the unit to control wind dispersal.

Standards promulgated in 40 CFR Section 264.272 (a) and (c) (2) specify that to obtain a full-scale permit, a demonstration must be performed to show that any hazardous constituents contained in the waste to be land applied must be completely degraded, transformed, or immobilized in the soil treatment zone. (The treatment zone is defined in Section 264.271 as no more than 5 feet (1.5 m) depth from the initial soil surface, and more than 3 feet (1 m) above the seasonal high water table.) If the applicant is required to use field or laboratory analyses or tests to conduct an LTD, these tests, which involve the treatment and disposal of hazardous waste, can only be performed under a treatment demonstration permit.

The preamble to the Part 264 regulations (Federal Register, 47, No. 143, pp. 32326-7, July 26, 1982) explains land treatment requirements more fully:

> The basic criterion used in evaluating a treatment demonstration is that it must be possible to achieve complete degradation, transformation or immobilization of the hazardous constituents in a waste if that waste is to be applied at the unit. Within the limits of the tests used in the demonstration, this is a standard that requires 100% treatment. EPA believes that land treatment should be limited to wastes for which complete treatment is possible: therefore, the "100% treatment" criterion is most appropriate. EPA recognizes that it will not always be possible to achieve 100% treatment at an operating unit because of variations in climatic and

other conditions not fully under the control of the owner or operator. Thus, the failure to achieve 100% treatment at an operating unit does not necessarily constitute a permit violation but rather will often be grounds for modifying permit conditions to maximize the success of treatment at the unit.

The regulations also recognize the probabilistic nature of the demonstration in Section 264.272 (c) (2) in requiring that an LTD "be likely to show" complete degradation, transformation or immobilization. Any demonstration cannot guarantee complete treatment beyond the conditions of the test. The regulations also suggest that statistical testing of significance may be necessary to evaluate a treatment situation.

Other sections of Section 264 Subpart M standards for land treatment are relevant to the performance of an LTD. Part 264.278 presents a protocol for unsaturated zone monitoring at a full-scale facility. The unsaturated zone monitoring information from a reconnaissance survey or from an LTD utilizing field testing should be comparable to data generated in full-scale operation. If food chain crops are to be grown on a land treatment area, the LTD should be designed to include considerations given in Section 264.276. Treatment of ignitable or reactive wastes in an LTD must meet the criteria in Section 264.281. The LTD should approximate the design and operational requirements for full-scale operation of a land treatment facility under Section 264.273.

1.4 ADMINISTRATIVE OPTIONS FOR LAND TREATMENT DEMONSTRATIONS

Administrative procedures allow applicants to choose one of three permit approaches:

(1) an immediate full-scale facility permit

(2) a short-term treatment demonstration permit followed by a full scale facility permit; or

(3) a two-phase permit.

Full-scale, short-term, and two-phase permits are described in 40 CFR Section 270.63. Table 1.5 outlines the essential elements of these permit approaches, and the content of applications for each of these types of permits is described in Table 1.6.

An applicant with an existing interim status land treatment unit may apply directly for a full-scale facility permit if complete treatment can be demonstrated based on available literature data, additional reconnaissance data, and/or existing operating data. This approach requires documented historical records and intensive historical soil and waste characterization data that allow reliable retrospective extrapolations and conclusions regarding the treatment of individual hazardous constituents. Because ISS facilities are "treated as though they have been issued permits" (while awaiting completion of the Part 264 permitting process), field monitoring on hazardous wastes already applied at the facilities may be conducted (i.e., a reconnaissance survey of existing conditions). However, these tests must not

Table 1.5 Land Treatment Permit Elements (U.S. EPA 1984a)

Full-Scale Facility Permit

- Used when complete data have been collected to satisfy the treatment demonstration requirement (i.e., using available literature data, operating data, and/or lab or field test results).
- Contains provisions necessary to meet all the Subpart M, Part 264 requirements and all other applicable Part 264 standards.
- Requires a 45-day public comment period and hearing if requested or required under state regulations.

Short-Term Treatment Demonstration Permit

- Involves small-scale lab or field experiments to demonstrate that hazardous constituents in a candidate waste can be treated in the land treatment unit.
- Used when insufficient treatment information exists to satisfy treatment demonstration requirements for full-scale facility permits or to establish preliminary Phase 2 (full-scale) conditions for a two-phase permit.
- Contains provisions necessary to meet the general performance standards in Section 264.272(c).
- Requires a 45-day public comment period and hearing if requested or required under state regulations.

Two-Phase Permit

- Combination of above two permits when Phase 1 is for the treatment demonstration and Phase 2 is for the full-scale facility design and operation.
- Used when substantial but incomplete "treatment" data exists and when sufficient data are not available to completely satisfy a treatment demonstration, but are available to determine the preliminary set of full-scale facility permit conditions.
- Used when Phase 1 and 2 permits are based on substantial but incomplete information; Phase 2 permit is modified to incorporate the results of Phase 1.
- Avoids the burden of two separate permitting procedures (e.g., only one public comment and hearing is necessary rather than two) unless a major permit modification is required (Part 124 and 47 FR 32335).
- Contains provisions necessary to meet treatment demonstration (Phase 1); contains provisions to meet all applicable Part 264 standards (Phase 2).

Table 1.6 Permit Application Content for Each Permit Element (U.S. EPA 1984a)

Full-Scale Facility Permit

- Information addressing the general standards applicable to all facilities - Part 270.14, "General Information Requirements."
- Information requirements of Part 270.20 addressing the Subpart M, Part 264 requirements
    - -- Treatment Demonstration Plan and Results
    - -- Land Treatment Program
    - -- Design and Operating Requirements
    - -- Food Chain Crops
    - -- Closure and Post-Closure Care
    - -- Ignitable and Reactive Waste
    - -- Incompatible Wastes
- Information addressing the groundwater protection requirements in Subpart F, Part 264.

Short-Term Treatment Demonstration Permit

- Treatment demonstration plan including provisions to meet the Part 264.272(c) performance standard: any field or laboratory test conducted must
    - -- simulate characteristics of the proposed land treatment unit, including waste, climate, topography, treatment zone soil, and operating practices to be used at the unit;
    - -- be likely to show that hazardous constituents will be completely degraded, transformed, or immobilized in the treatment zone; and
    - -- be conducted in a manner that protects human health and the environment considering waste characteristics, operating and monitoring measures, test duration, waste volume used in the test, and, in the case of field tests, the potential for migration of hazardous constituents to groundwater or surface water.
- Certification of completion of LTD and results submitted to the appropriate regulatory agency(ies) at end of study and as part of full-scale facility permit application.

Two-Phase Permit

- Same as full-scale facility permit except that the results of the short-term treatment demonstration are submitted (Phase 1).

be carried out in a manner that will lead to violation of the Part 265 interim status standards. If the testing involves new application of wastes, a permit (short-term or two phase) must be obtained.

If literature data are to be useful and supportive of an LTD at an ISS facility, the data should have been generated under conditions similar to those at the proposed unit. The literature information should include specific data on the fate and movement of hazardous constituents (i.e., compounds listed in Appendix VIII of 40 CFR Part 261) present in the waste under conditions representative of the site (soil, temperature, moisture, hydraulic conductivity, etc.) proposed to be used. Although literature data may assist in the design of the laboratory and field tests, these data alone are not expected to fully satisfy the requirements of a treatment demonstration. As the data base improves with continued research, literature data may become more useful.

Evidence of the use of operation and/or management practices that maximize treatment performance, as required in 40 CFR Section 264.273, must also be presented with an interim status land treatment facility permit application. If no operation and/or management practices have been utilized for treatment maximization laboratory or field investigations may be required at the discretion of the permit writer.

The short-term treatment demonstration permit, usually applied for by new units, existing units with contamination, or existing units that are planning to treat new wastes or implement major design and operational changes, authorizes field testing or small-scale laboratory testing, and contains provisions necessary to meet the general performance standards in Section 264.272 (c) (see Table 1.6). The applicant only submits a treatment demonstration plan in the permit application. An applicant should apply for this permit when insufficient treatment information exists (1) to fully satisfy the treatment demonstration for a full-scale permit without additional testing or investigation; or (2) to establish preliminary permit conditions for the full-scale facility in a two-phase permit. A 45-day public comment period is required prior to permit issuance. The public may request a hearing, if they desire. After the laboratory or field tests are completed and are found acceptable, the applicant should apply for a full-scale facility permit. The full-scale permit is used when complete data have been collected to satisfy the treatment demonstration. The applicant should submit both the treatment demonstration plan and results, as well as all other information described in Table 1.6, for application for a full-scale facility permit.

The two-phase permit is a combination of the short-term permit and full-scale facility permit. Phase 1 of the permit includes conditions for the short-term treatment demonstration, while Phase 2 includes provisions for the full-scale facility design and operation. This permit should be used when substantial but incomplete data exist to satisfy the treatment demonstration, but sufficient data are available to determine the preliminary full-scale facility conditions. For the two-phase facility permit, the applicant submits the same information as for the full-scale facility permit, except that the results of the short-term treatment demonstration (Phase 1) are submitted at a later date. Thus, the permitting official first writes a draft permit for

Phases 1 and 2, and then after the results of the treatment demonstration are submitted, modifies the Phase 2 permit as required. The primary advantage of the two-phase permit is the elimination of the need for two separate permitting procedures, i.e., one for the treatment demonstration and another for the full-scale facility permit.

After the two-phase permit is issued, Phase 1 is effective during the period of the treatment demonstration. Phase 1 of the permit is only applicable to laboratory and field studies, and the interim status of the remainder of the HWLT unit is unaffected. The owner/operator may continue to operate under interim status on this remaining area during the demonstration. The owner/operator is subject to enforcement action if interim status violations occur in the remaining area.

The owner/operator should submit the following to the permitting authority after completion of the tests: (1) a certification that the LTD tests have been performed in accordance with Phase 1 of the permit; and (2) all of the data collected during the LTD, along with interpretations and suggestions for adjustments in the final design, operation, and management plans that will be incorporated in the full-scale facility permit.

The permitting authority will evaluate the results and will modify as required the second phase of the permit to incorporate the LTD results. Phase 2 of the permit (i.e., full scale operation) will become effective after any and all minor modifications are completed.

Guidance for minor modifications are given in Section 270.42(m) and (n), which states that minor modifications may only:

> (m) Change any conditions specified in the permit for land treatment units to reflect the results of the field tests or laboratory analyses used in making a treatment demonstration in accordance with Part 270.63, provided that the change is minor;
>
> (n) allow a second treatment demonstration for land treatment to be conducted when the results of the first demonstration have not shown the conditions under which the waste or wastes can be treated completely as required by Section 264.272(a), provided that the conditions for the second demonstration are substantially the same as the conditions for the first demonstration.

If the information from the LTD necessitates major changes in the Phase 2 permit, the permit may be modified or revoked and reissued under guidelines given in Section 270.41. If a determination is made that the permitted activity endangers human health or the environment, the permit may be terminated(Section 270.43).

1.5 CRITERIA FOR CHOOSING A LAND TREATMENT DEMONSTRATION SCENARIO

The choice of an appropriate LTD approach involves organizing information and comparing that information with several criteria (Figure 1.2). The first question to address is whether the land treatment unit is new or existing. An existing unit is one where waste has been previously applied. For the purposes of conducting an LTD, the unit is considered "new" only if it has not had previous waste application.

1.5.1 Evaluation of Adequacy of Part B Information for Definition of LTD Plan (Existing Sites)

By November 8, 1985 existing sites under interim status should have submitted a Part B application for a permit or have indicated their intention to close. The Part B permit application should provide a description of procedures that will be used to demonstrate complete degradation, transformation, and immobilization of hazardous constituents in the land treatment unit (see Appendix A). As part of this description, the collection of the following information is recommended:

- Waste characterization, including organic and inorganic, Appendix VIII hazardous constituents, and other waste constituents and properties that may affect the performance of the land treatment unit
- Past waste management activities
- Site and soil survey information
- Waste distribution in the soil
- Soil-pore liquid monitoring
- Groundwater monitoring, including data collected during Part 265 Subpart F monitoring program and if applicable, data collected according to the regulations given in Section 270.14(c)(4)

If any or all of this information is not available, the applicant in conjunction with the permit writer should design and conduct a reconnaissance survey to obtain the missing data, according to the guidelines given in

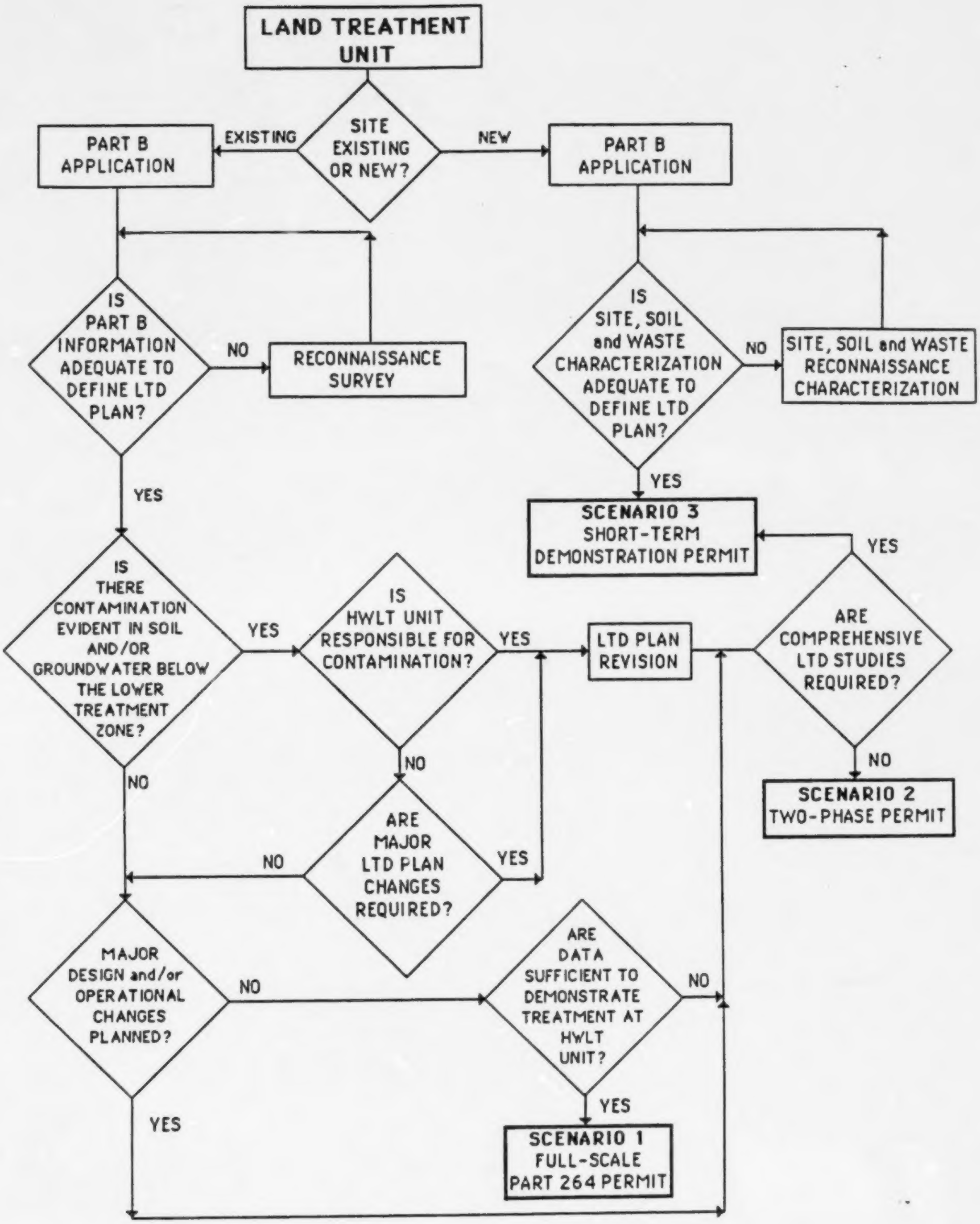

LAND TREATMENT UNIT
SITE EXISTING OR NEW?
EXISTING
NEW
PART B APPLICATION
PART B APPLICATION
IS PART B INFORMATION ADEQUATE TO DEFINE LTD PLAN?
NO
RECONNAISSANCE SURVEY
IS SITE, SOIL and WASTE CHARACTERIZATION ADEQUATE TO DEFINE LTD PLAN?
NO
SITE, SOIL and WASTE RECONNAISSANCE CHARACTERIZATION
YES
SCENARIO 3 SHORT-TERM DEMONSTRATION PERMIT
YES
IS THERE CONTAMINATION EVIDENT IN SOIL AND/OR GROUNDWATER BELOW THE LOWER TREATMENT ZONE?
YES
IS HWLT UNIT RESPONSIBLE FOR CONTAMINATION?
YES
LTD PLAN REVISION
ARE COMPREHENSIVE LTD STUDIES REQUIRED?
YES
NO
SCENARIO 2 TWO-PHASE PERMIT
NO
NO
ARE MAJOR LTD PLAN CHANGES REQUIRED?
NO
YES
MAJOR DESIGN and/or OPERATIONAL CHANGES PLANNED?
NO
ARE DATA SUFFICIENT TO DEMONSTRATE TREATMENT AT HWLT UNIT?
NO
YES
SCENARIO 1 FULL-SCALE PART 264 PERMIT
YES

Figure 1.2 LTD guidance for selection of appropriate scenario.

Chapter 3 concerning the suggested types of information and procedures for data collection.

Part 265 regulations do not require data to be collected on Appendix VIII hazardous constituents. However, the analysis of these constituents are required for the LTD under Parts 270 and 264 for wastes, soil-cores, soil-pore liquid in the treatment and below treatment zones (if available) and groundwater and should be provided for the LTD review.

1.5.2 Contamination Below the Treatment Zone or in the Groundwater beneath the HWLT Unit

If the information presented for definition of the LTD plan indicates contamination with hazardous constituents below the treatment zone, as compared to a background area further evaluation of the site are necessary to determine required modifications to the LTD plan.

Indicators of contamination may include: (1) The unsaturated zone monitoring data (including soil core and soil-pore liquid data) collected during interim status and included in the operating record, as required under Section 265.73, which should demonstrate no significant migration of hazardous constituents below the treatment zone; (2) Data provided for the Part B permit application, i.e., data collected according to Part 265 Subpart F and Section 270.14(c)(4) guidance, which should be evaluated and compared to background data, using appropriate statistical techniques according to U.S. EPA groundwater sampling guidance; and (3) reconnaissance sampling data (including soil core and soil-pore liquid data and results of groundwater monitoring, which should demonstrate no significant increase of hazardous constituents (Appendix VIII) below the proposed treatment zone, within the active portion of the site, compared to background levels.

If the soil below the treatment zone or the groundwater is determined to be contaminated, an evaluation should be made whether the contamination is reasonably expected to come from the LT unit. If the LT unit is suspected as the contaminant source, further studies should be conducted. These studies may include deeper soil core sampling, either at specified intervals below the treatment zone to the top of the aquifer, or samples composited through depth increments to the top of the aquifer. ISS sites may show groundwater contamination below land treatment units due to either regulated or solid waste management units not associated with the land treatment units.

Analytical problems may occur due to different detection limits for hazardous constituents in the different sampling media, e.g., detection limits may be lower in soil-pore liquid than in soil core samples, thus indicating contamination that may not even be detected in the soil core samples. An organic environmental chemist should be consulted if such analytical problems are suspected.

If the groundwater is contaminated due to the HWLT unit, major revisions to the LTD plan will likely be necessary. Revisions may also be necessary if only the soil below the treatment zone is contaminated. If minor contamination is found in the below treatment zone soil (e.g., only in one or a few sample locations, or only minor contamination levels are found), the LTD may possibly be conducted on the uncontaminated portions of the HWLT unit. Changes in loading rate, frequency of application, or method of application may be evaluated in the LTD to enhance treatment.

If the site is highly contaminated beneath the treatment zone, the performance of an LTD field study may not be technically feasible. Prior contamination of the site would likely be difficult to distinguish from new applications of the waste, unless radioactive tracers were used.

The regulatory agency may pursue legal action based on demonstrated groundwater contamination at an ISS HWLT unit. The HWLT unit may be required to cease operations in the contaminated area if necessary to protect human health and the environment. The facility may decide not to proceed with an LTD or may decide on a more comprehensive LTD design. However, at the present time RCRA regulations do not require prior clean-up of a site before LTD studies can be conducted.

For sites requiring only minor modifications to the LTD design due to below treatment zone soil contamination, there is a possibility that further laboratory or field studies may not be required.

1.5.3 Major Design and Operational Changes in the HWLT Unit

For an existing HWLT unit to be permitted on the basis of current design and management, the planned future activities under a Part 264 permit should involve similar wastes, similar waste application rates and methods of application, similar management practices, and should continue to use the same soil as the treatment medium. If current and proposed future activities are not similar, the planned changes should lead to more conservative application rates, better waste quality (i.e., lower concentrations of hazardous or pertinent nonhazardous constituents), or better management practices or design. In addition, for permitting on the basis of current design and management practices, the soils presently used cannot be replaced by others. To demonstrate future consistency of operation, the permit application should address planned unit processes, waste application rates, and use of the site soil. If major design and operational changes are planned, the LTD should be more comprehensive and conducted according to Scenario 2 or 3.

1.5.3.1 Planned Unit Processes--

Major changes in the unit processes generating the wastes are of concern if the changes result in the introduction or increase of measurable amounts of hazardous constituents in the waste or the production of a new waste stream. New constituents introduced after a treatment demonstration would not have been tested in the treatment demonstration, and therefore their behavior in the HWLT unit would not be definitively known. Later changes in unit process design and/or operation may or may not warrant a new LTD, depending on whether changes may be anticipated to adversely affect the performance of a land treatment unit.

The relative abundance of various waste constituents in even a single waste stream may be expected to vary due to seasonal effects, fluctuations in feed stocks, relative market demand for the various products of the waste generator, and intermittent batch generation of certain wastes. These variations may be accounted for in reconnaissance waste characterization. However, the on-going waste monitoring program should be capable of detecting substantial long-term changes in waste quality. For the LTD, anticipated changes that could affect waste quality should be identified. If these changes may be anticipated or are shown to adversely affect the performance of a land treatment unit, Scenario 2 or 3 should be used.

1.5.3.2 Planned Waste Application Rates--

The applicant may wish to investigate waste application rates higher than currently used in practice due to forecasted increases in the rate of production for one or several waste streams or a change in the composition of the waste stream due to operational changes (e.g., application of a dewatered waste stream will result in an increased application rate of hazardous constituents compared to the same application of the waste stream that has not been dewatered; however, dewatered sludge may be applied to the land treatment unit at a lower loading rate so that the concentration of hazardous constituents in the soil remains the same as the concentration resulting from the application of nondewatered sludge). Planned application rates should be expressed in terms of the concentrations and application rates of limiting constituents, or constituents that are nearly limiting, as well as in terms of less descriptive parameters, such as oil content.

Scenario 2 or 3 should be followed if increases in the application rate(s) are anticipated for the future.

1.5.3.3 Planned Use of Soils--

The use of a different soil for the land treatment unit may significantly affect the behavior and fate of waste constituents within the treatment zone. Due to differences among the physical, chemical, and biological properties of soils, treatability of waste within different soils likewise varies (U.S. EPA 1983a). An expansion of the HWLT unit onto a different soil series would be considered a change in treatment medium and would require the performance of a more rigorous LTD, i.e., the use of Scenario 2 or 3. Likewise, removal and replacement of soil present on an existing active area with soil from a different series is also regarded as a change of treatment medium and would indicate the use of Scenario 2 or 3.

Finally, a proposed major disruption of the treatment zone would significantly alter soil conditions. While normal operations are expected to disrupt only surface soils in the zone of incorporation, major disruption involves one of the following: deep tillage (e.g., greater than 18 inches), an activity which mixes the lower portion of the soil profile that normally would remain undisturbed during HWLT operations, or the artificial drainage and lowering of a seasonal high water table that had previously encroached into the treatment zone in order to meet the separation requirements of 40 CFR Section 264.271 (c) (2). These types of activities would require the use of Scenario 2 or 3 for the LTD.

1.5.3.4 Guidance on Planned Design and Operation--

Management personnel of the facility should be consulted to determine possible near-term modifications to the waste streams or land treatment unit.

Table 1.7 lists information needed to assess planned design and operational changes and presents guidance in interpreting this information. For anticipated future changes, a decision must be made whether to conduct the LTD for the revised unit at the present or at a later time. If design and operational changes will occur, HWLT unit permitting as per Scenario 2 or 3 may be used.

Table 1.7 Information Required to Assess Planned Changes in Design and Operation and to Assess the Suitability of the Use of Scenario 2

Category	Confirmation of No Design and Operational Changes
Unit Processes	No anticipated measurable quantities of additional hazardous constituents that are not presently in the waste. No new wastes proposed for treatment.
Waste Application Rates	No significant increase in the quantities of hazardous constituents applied per unit area per unit time (kg/ha/yr).
Soil	No expansion onto new soil series; no importation of different soils for use as the treatment medium; no major disruption of existing soils.

1.5.4 Evaluation of Whether Information is Sufficient to Demonstrate Treatment at the HWLT Unit

If only literature, reconnaissance, and existing operating data form the basis for a full-scale facility permit, the applicant is limited to waste application rates and frequencies used during past operations in succeeding full-scale operations (i.e., the applicant may not have the opportunity to evaluate higher loadings or frequencies on a full-scale operating basis). Also, because this approach is a retrospective analysis, sufficient information on the relative mobility and degradation of hazardous constituents based on monitoring data will likely not be available for determination of the "principal hazardous constituents" (PHCs) that may serve as indicators in unsaturated zone monitoring (UZM) during full-scale operation. A number of parameter estimation methods are available that provide an estimate of constituent properties based on fundamental chemical and physical/structural characteristics (structure activity relationships (SAR), UNIFAC, correlation equations, etc.) (Lyman et al. 1982). These methods are limited in terms of breadth of application and extent of verification and their use should be supported with some confirmatory data for the complex waste mixture to be land treated. In most cases, additional studies are required to provide sufficient data for the selection of appropriate PHCs. Therefore, an applicant with an ISS facility who uses laboratory studies or field investigations to complete the treatment demonstration should apply for an LTD permit (i.e., a short-term treatment demonstration followed by a full-scale facility permit, or a two-phase permit).

If information from ISS operating experience, literature data, and reconnaissance survey is not sufficient to demonstrate treatment, the performance of an LTD under an LTD permit is appropriate, i.e., requires the use of Scenario 2 or 3.

1.5.5 Further Information Requirements for Demonstrating Treatments

If the Part B information is judged "substantial but incomplete" by the permit writer, the applicant may conduct the LTD according to Scenario 2 (Figure 1.3), using a two-phase permit. Depending on the quality and completeness of information presented, the LTD may include only the quantitative presentation of complete, comprehensive reconnaissance data, past operating data, and estimated or laboratory determined waste constituent parameter data, and the evaluation of such data using the LTD model described in Chapter 4. If these data are still considered insufficient, additional laboratory analyses, and laboratory and field verification studies may be necessary. The permit writer and the applicant should determine the exact scope of the treatment demonstration using available operating, monitoring, and performance data in a pre-application meeting.

When there is not enough information to establish Subpart M permit conditions, Scenario 3 (Figure 1.4) should be followed, using a short-term demonstration permit. The technical approach to the performance of an LTD according to Scenario 3 involves the comprehensive assessment of the potential for migration of hazardous constituents, the potential for their degradation, immobilization, transformation, and detoxification, as well as the determination of loading rates and management practices for performance maximization at the land treatment unit. These endpoints are accomplished by the use of a combination of literature data, laboratory analyses, and laboratory and field verification studies.

A redesigned ISS unit with major design and operational changes planned, should follow Scenario 3 to obtain a permit. Major design and operational changes considered under Scenario 3 include: new wastes (wastes that have not been applied previously at the unit), changes in waste application rates, replacement or addition of soil for waste treatment at the unit, and/or major disturbance of the soil at the unit. Also, units that have exhibited contamination below the treatment zone are eligible for an LTD permit under Scenario 3.

1.5.6 LTD Approach for New Sites

Prior to beginning the LTD, the applicant with a new site should perform a site/soil survey to determine if the proposed site is suitable for land treatment, and a complete waste characterization to determine the presence of

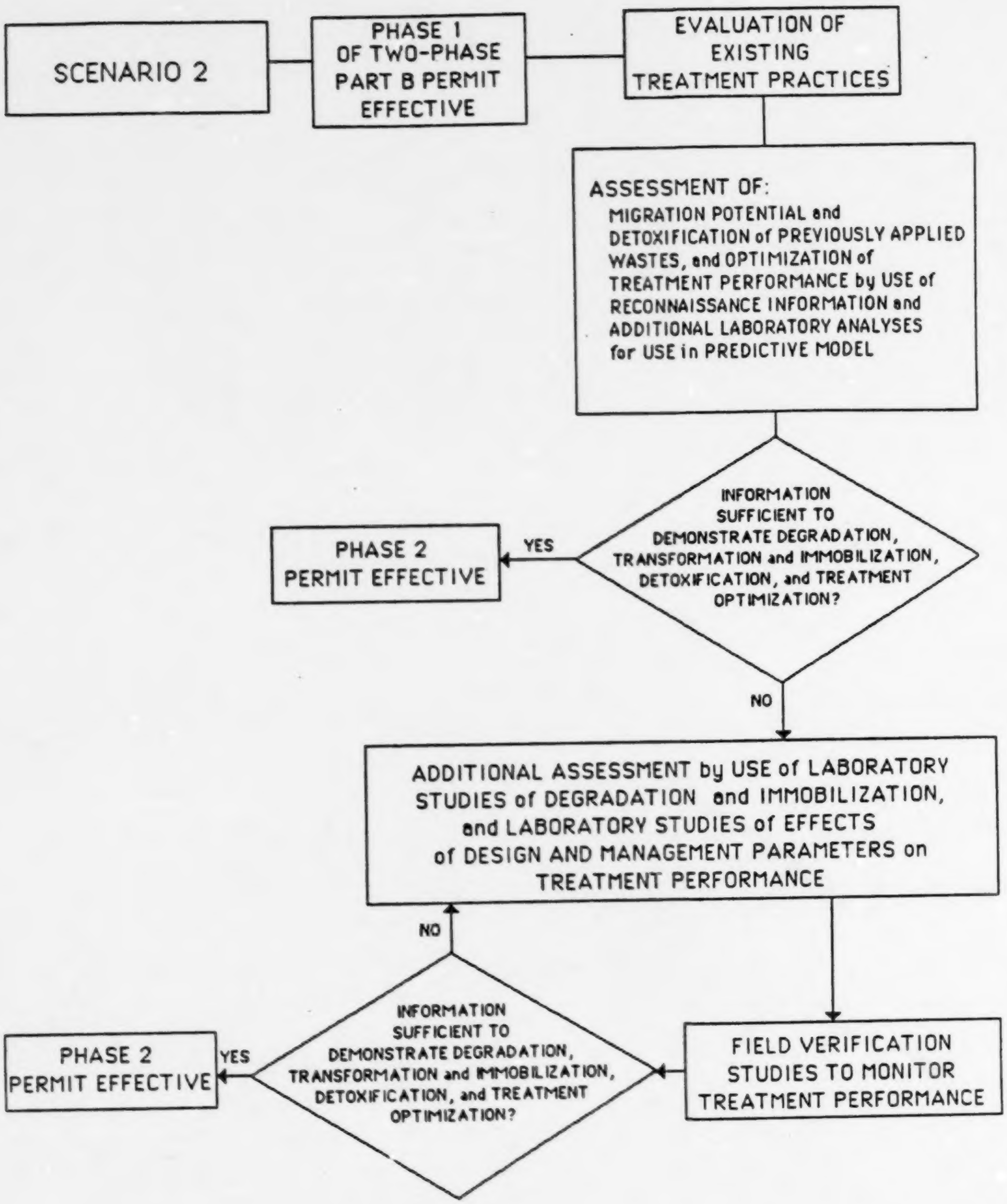

SCENARIO 2
PHASE 1 OF TWO-PHASE PART B PERMIT EFFECTIVE
EVALUATION OF EXISTING TREATMENT PRACTICES
ASSESSMENT OF: MIGRATION POTENTIAL and DETOXIFICATION of PREVIOUSLY APPLIED WASTES, and OPTIMIZATION of TREATMENT PERFORMANCE by USE of RECONNAISSANCE INFORMATION and ADDITIONAL LABORATORY ANALYSES for USE in PREDICTIVE MODEL
INFORMATION SUFFICIENT TO DEMONSTRATE DEGRADATION, TRANSFORMATION and IMMOBILIZATION, DETOXIFICATION, and TREATMENT OPTIMIZATION?
YES
PHASE 2 PERMIT EFFECTIVE
NO
ADDITIONAL ASSESSMENT by USE of LABORATORY STUDIES of DEGRADATION and IMMOBILIZATION, and LABORATORY STUDIES of EFFECTS of DESIGN AND MANAGEMENT PARAMETERS on TREATMENT PERFORMANCE
FIELD VERIFICATION STUDIES TO MONITOR TREATMENT PERFORMANCE
INFORMATION SUFFICIENT TO DEMONSTRATE DEGRADATION, TRANSFORMATION and IMMOBILIZATION, DETOXIFICATION, and TREATMENT OPTIMIZATION?
NO
YES
PHASE 2 PERMIT EFFECTIVE

Figure 1.3. Specific guidance and information requirements for LTD meeting the definition for Scenario 2.

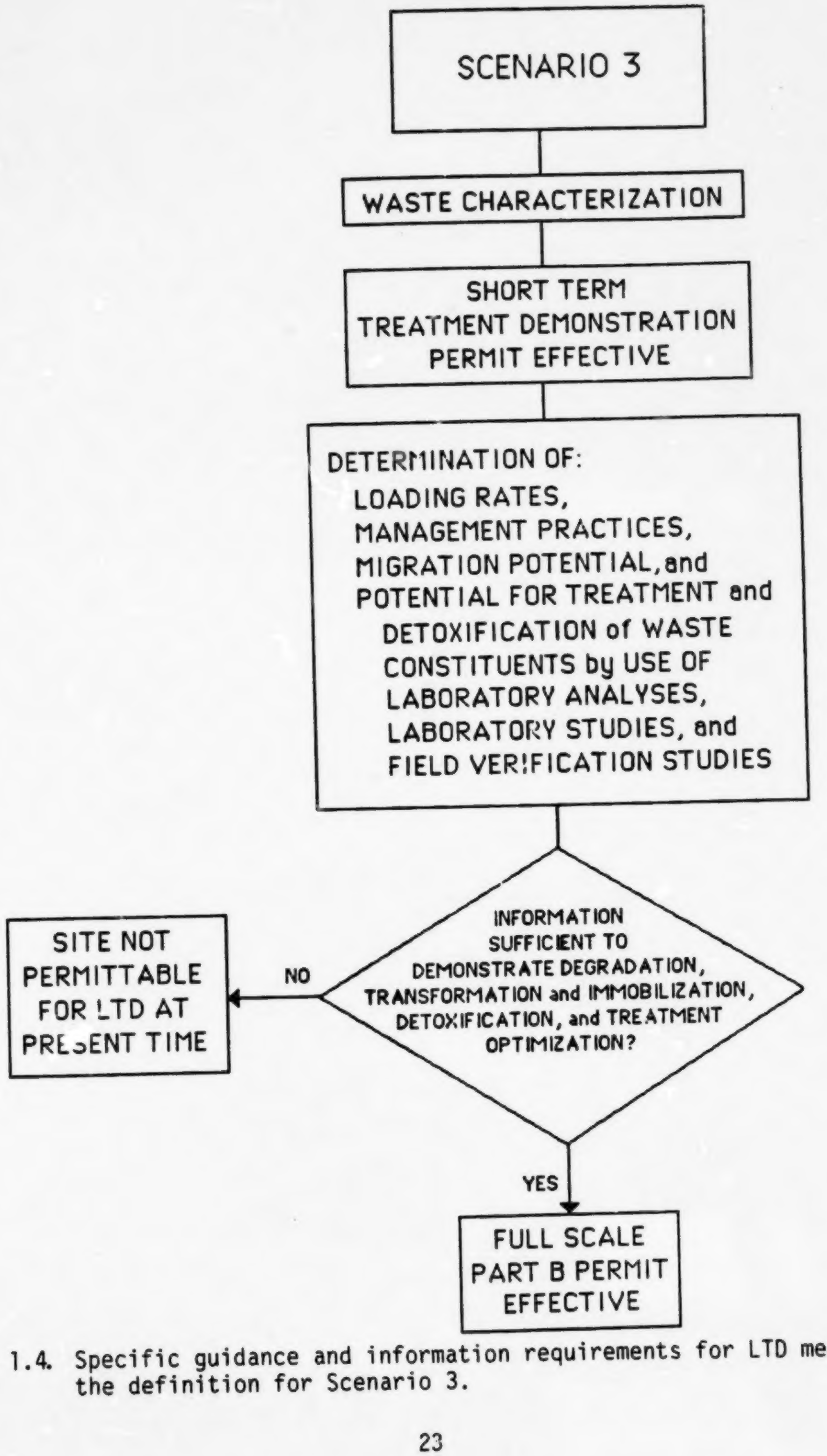

SCENARIO 3
WASTE CHARACTERIZATION
SHORT TERM TREATMENT DEMONSTRATION PERMIT EFFECTIVE
DETERMINATION OF: LOADING RATES, MANAGEMENT PRACTICES, MIGRATION POTENTIAL, and POTENTIAL FOR TREATMENT and DETOXIFICATION of WASTE CONSTITUENTS by USE OF LABORATORY ANALYSES, LABORATORY STUDIES, and FIELD VERIFICATION STUDIES
INFORMATION SUFFICIENT TO DEMONSTRATE DEGRADATION, TRANSFORMATION and IMMOBILIZATION, DETOXIFICATION, and TREATMENT OPTIMIZATION?
NO
SITE NOT PERMITTABLE FOR LTD AT PRESENT TIME
YES
FULL SCALE PART B PERMIT EFFECTIVE

Figure 1.4. Specific guidance and information requirements for LTD meeting of the definition for Scenario 3.

hazardous constituents and other pertinent constituents that may affect land treatment. Guidelines for assessing the suitability of a site for land treatment are given in the *Permit Writers' Guidance Manual for the location of Hazardous Waste Land Treatment Facilities: Criteria for Location Acceptability and Existing applicable Regulations* (U.S. EPA 1985b). The applicant then obtains a short-term demonstration permit according to Scenario 3 that incorporates the provisions necessary to meet the general performance standards in Section 264.272(c). A 45-day public comment period is required prior to permit issuance. The public may request a hearing if they desire. Once this permit is obtained, the LTD may begin. Once the LTD is completed, a certification of completion and a final Part B permit application incorporating the LTD results should be prepared. A full-scale Part 264 facility permit is issued after appropriate administrative steps are taken, including a second period for public comment and a public hearing.

1.6 IMPLICATIONS OF THE HAZARDOUS AND SOLID WASTE AMENDMENTS OF 1984 (HSWA) FOR LAND TREATMENT DEMONSTRATIONS AND FACILITIES

Although land treatment demonstrations are presently regulated under existing RCRA regulations (Section 264.271 et seq.), the recent HSWA have changed the regulatory approach to land disposal in general, and directly impact land treatment facilities and the performance of LTDs.

As Section 1002(b) (7) of the HSWA indicates, the U.S. Congress felt that certain classes of land disposal facilities could not assure long-term containment of certain hazardous wastes. While landfills and surface impoundments were the primary motivation for the amendments, land treatment was also defined as "land disposal" under Section 3004(k) and is subject to many of the stringent provisions of the HSWA. Some of the HSWA provisions that may relate to the performance of land treatment demonstrations are summarized here.

Sections 3004(d), (e), and (g) prohibit the land disposal of *all* hazardous waste unless (1) the waste is treated *prior to "land disposal"* in compliance with a treatment standard promulgated under Section 3004(m) or (2) if an interested party demonstrates, to a reasonable degree of certainty, that there will be *no migration* of hazardous constituents from the disposal unit or injection zone for as long as the waste remains hazardous. Sections 3004 (d), (e), and (g), as well as a schedule published by the EPA (51 FR 19300, May 28, 1986), establish a schedule for implementing the land disposal prohibitions for hazardous wastes.

Section 3004(n) requires that the U.S. EPA promulgate regulations concerning air emissions from land disposal facilities. Currently U.S. EPA is conducting studies to evaluate the potential level of hazardous volatile organics released from land disposal facilities. However, this LTD Guidance Manual does not address the collection of site-specific information for this evaluation since air standards have not been promulgated at this time.

Section 3004(o) requires new land treatment units to have EPA-approved leak detection systems. Although this requirement does not take effect until the regulations are issued, the performance of LTDs may provide opportunities to evaluate the suitability of unsaturated zone sampling and analysis techniques to meet this requirement.

Section 3004(u) requires corrective action for all releases of hazardous waste or constituents from any solid waste management unit at a treatment, storage, or disposal facility seeking a permit, regardless of the time at which the waste was placed in the unit. The Agency has determined that Section 3004(u) should not apply to land treatment demonstration permits issued pursuant to Section 270.63(a)(2), because these permits generally act as an extension of the application process by providing information for the final permit. The requirements of Section 3004(u) must be incorporated into the final Part B permit for such facilities. Similarly, the requirements of Section 3004(u) must be addressed in the second phase of a two-phase permit issued under Section 270.63(a)(1).

Section 3004(v) requires cleanup beyond the property boundary for permitted facilities. The U.S. EPA has required that corrective actions be undertaken as soon as possible. If groundwater monitoring indicates contamination at a land treatment site performing an LTD, some form of corrective action may also be required. From a technical standpoint, this manual recommends that such corrective actions be taken before a facility defines an LTD on an ISS land treatment site. A facility applying for a Part B permit and having groundwater contamination may be required to concurrently plan for corrective action responses as well as fulfilling other Part B requirements.

CHAPTER 2

TECHNICAL APPROACH TO THE PERFORMANCE OF AN LTD

2.1 EVALUATION OF TREATMENT PROCESS

For each candidate waste that will be applied at a land treatment unit, the owner or operator must demonstrate that hazardous constituents in the waste can be completely degraded, transformed, or immobilized in the treatment zone. The technical approach to the demonstration of land treatment is organized to address the evaluation of degradation, transformation, and immobilization processes within the context of each scenario presented in Chapter 1 of this manual.

Table 2.1 identifies specific measurements used to evaluate the principal processes involved in land treatment that were identified above. For example, measuring the concentrations of hazardous constituents in the treatment zone soil through time may be used to assess the degradation potential of the waste. Similarly, leaching potential may be observed by comparing the mass of hazardous constituents in the soil-core with the mass in the soil-pore liquid, either in the laboratory or in the field. Leaching potential may also be evaluated through measuring and comparing concentrations of hazardous constituents in field plots below the treatment zone with background concentrations. Toxicity testing can be used in laboratory and field experiments to assess the transformation of hazardous constituents through measuring relative detoxification with time. Table 2.1 also identifies the sources of information for evaluating each treatment process, type of sample, and analytical methods for evaluation of each treatment process. Tests for identifying the statistical significance for each of the treatment processes based on literature, laboratory, and field generated data are appropriate, and are presented in Appendix B of this guidance manual.

As indicated in Table 2.1, the requirement for demonstrating treatment, i.e., degradation, transformation, and immobilization, can be addressed using several approaches. Information concerning each treatment process can be obtained from several sources including literature data, field tests, laboratory studies, laboratory analyses, theoretical parameter estimation methods, or in the case of existing units, operating data (40 CFR Section 264.272) as indicated in Table 2.1.

Literature data used to support the LTD should be clearly documented with respect to waste type, waste toxicity, soil characteristics, and environmental variables including temperature. Theoretical parameter estimation methods for determination of degradation and immobilization information (partitioning in the soil/waste mixture) also should be clearly documented and justified as the

Table 2.1 Monitoring and Evaluation Strategies to Assess Treatment Processes in a Land Treatment Demonstration

Treatment Processes	Monitoring and Evaluation Measurement	Sources of Information	Type of Sample	Analytical Methods
Degradation	Change in concentration of principal organic hazardous constituents over time in the treatment zone soil (TZ)	Laboratory Kinetic Study Field Plot Study Literature Values	Waste & TZ[*] Soil-core Waste & TZ Soil-core	Type II Type II
	Change in concentration of indicatory parameters over time (e.g., oil content, benzene extractables)	Laboratory Kinetic Study Field Plot Study ISS Operating Data Literature Values	Waste & TZ Soil-core Waste & TZ Soil-core Waste & TZ Soil-core	Type I Type I Type I
	Potential for degradation/leaching	Mathematical Model	Waste & TZ Soil-core	
Transformation	Concentration of hazardous metabolites or chemical breakdown products	Field Plot Study Reconnaissance Study Laboratory Study	Waste & TZ Soil-core Waste & TZ Soil-core Waste & TZ Soil-core	Type III Type III Type III
	Change in toxicity over time	Field Plot Study Laboratory Analysis	TZ Soil-core, Waste, & Soil-Pore Liquid	Toxicity Tests Toxicity Tests
Immobilization	Decrease in pollutant velocity relative to soil-pore liquid velocity or air velocity, measured by comparing soil core with soil-pore liquid concentrations of hazardous constituents	Field Plot Study Reconnaissance Study	TZ Soil Cores & Soil-pore Liquid TZ Soil Cores & Soil-pore Liquid	Type III Type III
	Buildup in concentration of metals over time	Field Plot Study Reconnaissance Study ISS Data	Waste & TZ Soil-core Waste & TZ Soil-core Waste & TZ Soil-core	Type II Type II Type II
	Concentration of Appendix VIII compounds below the treatment zone (BTZ) (leaching)	Field Plot Study Reconnaissance Study	BTZ[†] Soil Cores, Soil-pore Liquid & Groundwater	Type III Type III
	Potential for leaching/degradation	Mathematical Model	Waste & TZ Soil-core	

[*] TZ = Treatment zone.
[†] BTZ = Below treatment zone.

approach selected. Also, an assessment of the quality of the data should be given. Quality of literature data may be assessed based on criteria including statistical approach, results of statistical analyses (confidence limits, coefficient of variation, precision, etc.), and rigorousness of experimental design. The U.S. EPA considers the use of literature information alone as insufficient to support an LTD at the present time.

Field tests may include sampling of the treatment zone soil, soil-core and soil-pore liquid below the treatment zone, and groundwater sampling. A statistical approach to field sampling and evaluation of analytical results is recommended. Information concerning statistical approaches and techniques are included in Appendix B of this guidance manual. Also Chapters 3 and 6 of this manual provide detailed information concerning reconnaissance and field verification studies, respectively, as sources of information for assessing treatment (degradation, transformation, and immobilization). Chemical and bioassay techniques are discussed in this chapter and in Chapter 5. Field verification studies may be based on results of the mathematical model assessment of design and management parameters.

Laboratory studies, laboratory analyses, and soil/waste characterization also provide information concerning treatment effectiveness for design and management combinations, and are identified in the scenarios presented in Chapter 1. A laboratory study involves the use of controlled and experimental treatments where treatment results are compared in order to select the design/management combination that maximizes treatment, i.e., the best set of SSACs for all hazardous constituents in the waste. Laboratory analyses within the context of the scenarios refers to the determination of degradation rates and partition coefficients for input into the land treatment mathematical model. Waste and soil characterization refer to any bioassay(s) and/or chemical procedure(s) or test(s) that are used to determine the treatment status of a specific sample. Laboratory studies therefore include laboratory analyses and waste/soil characterization in the format of an experimental matrix for evaluating the effectiveness of design/management combinations, and for selecting the design/management combination that maximizes treatment. The design/management combination chosen may then be used in the field verification study part of the LTD.

For existing units where operating data are used to support, the LTD the quality and amount of the data presented are important. Also, the planned future use of the LTD unit compared with historical design/management practices need to be evaluated. It is the philosophy of this manual that a combination of data sources should be utilized, e.g., literature data, laboratory analyses, laboratory studies and field verification tests, to strengthen confirmation of hazardous constituent treatment demonstration. The availability and completeness of existing operating and literature data will influence the need for collection of further performance data.

Evaluation of these treatment processes may be integrated through the definition and the determination of the soil/site assimilative capacity (SSAC). The SSAC is defined as the amount of waste that may be applied per unit of site-soil per unit of time, based on the individual hazardous constituents present. The SSAC is developed for a specific candidate waste and a specific design and operation combination. Therefore, the SSAC represents a combination of loading rate and loading frequency that allows complete degradation, transformation, and immobilization of hazardous constituents to be accomplished within the defined treatment zone.

Prior to the determination of the SSAC, a waste characterization is conducted in order to identify and quantify hazardous constituents that are present in the waste.

2.2 DETERMINATION OF THE SITE/SOIL ASSIMILATIVE CAPACITY (SSAC) FOR A CANDIDATE WASTE

Determination of the SSAC for a hazardous waste land treatment demonstration involves addressing the factors identified in 40 CFR 264.272 in an integrated manner:

(1) extent of immobilization;

(2) rate of biodegradation; and

(3) transformation/detoxification potential (effects on the soil treatment medium and potential public health aspects).

The toxicity of the waste or waste constituents to the treatment medium must also be evaluated to ensure that the biodegradation pathway is not eliminated.

Through the evaluation of the factors listed above, information required by RCRA for conducting an LTD, i.e., design and operation and management characteristics presented in Table 2.2, will be obtained and an assessment of the land treatability of a waste can be made.

Table 2.2 Design and Operation Parameters for LTDs

Design parameters	Operation and management
Waste application method	Soil moisture
Waste application rate(s)	Microbial activity
Waste application frequency	Chemical activity
	Soil pH

2.2.1 The Toxicity Component of the SSAC

The following list of bioassays identify those tests commonly cited in the professional literature to assess the impact of a waste on soil microbial activity:

1. Microtox toxicity assay
2. Carbon dioxide evaluation
3. Dehydrogenase activity
4. Nitrification
5. Microorganism plate count

Descriptions of each bioassay listed above and additional bioassays, and procedures, methods, and guidance on data handling and interpretation are detailed in Chapter 5 of this guidance manual. The bioassay or battery of bioassays selected for use in the LTD may be negotiated between the permit applicant and the permit writer and agreed in writing at the initiation of negotiations. Regardless of which assays are chosen, due to the inherent variability of biological testing procedures and the lack of a single assay which shows waste toxicity to all microbial functions, it is suggested that a battery of two or more assays be used to more confidently identify critical toxic loading rates.

2.2.2 The Immobilization Component of the SSAC

Evaluation of loading rates also involves an investigation of the extent of migration of hazardous constituents. The approach taken in this guidance manual is to recommend that the maximum loading rate that does not prohibit microbial degradation of readily biodegradable organic constituents in the waste be established and, using this maximum loading rate, that the immobilization of hazardous waste constituents by the site/soil at that loading rate be evaluated. Thus, the amount of waste on a given area per application is limited either by the acute toxicity to the treatment medium or by the mobility of waste constituents.

Mobility includes the downward transport, or leaching potential, of waste constituents. Several approaches for the evaluation of the mobility of a waste and specific hazardous waste constituents are listed below. These include:

1. predictive mathematical models
2. laboratory isotherm analyses
3. laboratory column studies
4. laboratory analyses for soil thin layer chromatography
5. field plot studies
6. barrel lysimeter studies
7. parameter estimation methods including structure-activity relationships, etc.

The downward transport, or leaching potential, of the waste is evaluated to ensure that waste constituents do not migrate out of the treatment zone.

Laboratory analyses and/or other methods may be used to determine partition coefficients, which are directly related to constituent immobilization. These constituent-specific partition coefficients can then be used as input parameters for the land treatment mathematical model (Chapter 4), along with biodegradation data, for estimating breakthrough concentrations and breakthrough times of hazardous constituents in the wastes. The collection and use of this immobilization data for identification of principal hazardous constituents (PHCs) and for field verification study design is described later in this chapter and in Chapter 5 "Laboratory Analyses and Laboratory Studies for Selecting Design and Operating Conditions."

2.2.3 The Biodegradation Component of the SSAC

The basis for biodegradation coefficient measurements is the determination of specific constituent soil concentrations as a function of time. One critical aspect of biodegradation measurements that should be emphasized is the deficiency in the measurement of biodegradation as the "apparent loss" of hazardous constituents over time. A biodegradation correction factor is required to adjust "apparent loss" rates that are appropriate to biodegradation. Experimental methods for the determination of a biodegradation rate for hazardous waste constituents are provided in Chapter 5 of this guidance manual. Corrected coefficients for biodegradation may represent a more accurate description of true biodegradation occurring within the land treatment unit, and may provide an improved estimate of the relative effect of different design/management options on constituent degradation and transport expected on a full-scale unit when they are used in conjunction with the land treatment mathematical model.

2.2.4 The Transformation/Detoxification Component of the SSAC

Information concerning the decrease in acute toxicity of the waste/soil mixture to soil microorganisms with time can be evaluated using short-term bioassay procedures for toxicity determination. The relative detoxification (transformation) of the waste by the treatment medium may be correlated with parent compound degradation to ensure protection of the public health (CFR Section 264.272(3) and soil microbial activity in the land treatment unit.

If parent constituents in a waste to be land applied are identified as having mutagenic or carcinogenic characteristics, it is recommended that a test be used to indicate the mutagenic potential of the leachate at the bottom of the treatment zone. A list of short-term bioassay that have been used to screen mutagenic characteristics of soil/waste mixtures include:

1. Salmonella typhimurium mammalian microsome mutagenicity assay (Ames assay);

2. Bacillus subtilis; and

3. Aspergillus nidulans

These assays have been used by K. W. Brown (1984) for assessment of the mutagenic potential and mutagenic detoxification of hazardous waste-soil mixtures. The Ames assay has also been used by Sims (1984) in laboratory and field treatability studies for assessment of deactivation of mutagenic characteristics for hazardous waste-soil mixtures. As with the toxicity assays, however, the above list is not comprehensive, and other methods for indicating detoxification may be used if their methodology, validity, etc., are substantiated for the LTD permit writer.

2.2.5 Calculation of the SSAC

The site/soil assimilative capacity is calculated as the integrated effects of degradation and immobilization of hazardous constituents present in the candidate waste, where treatment is not limited by toxicity and/or transformation/detoxification potential. In order to integrate information concerning degradation and immobilization, a mathematical model may be used to evaluate the SSAC and the effects of operation and management practices on the SSAC. A proposed land treatment model is described in detail in Chapter 4 and in Appendix C of this manual. The model is based on the model developed by Dr. Thomas Short, Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, for use in determining which hazardous substances should be banned from land treatment. The model allows for the evaluation of degradation and leaching potential of waste constituents in accordance with 40 CFR Section 264.272 in order to meet the requirements of Sections 264.271 and 264.273.

2.2.6 Principal Hazardous Constituents (PHCs)

The approach to demonstrating complete degradation, transformation, or immobilization of hazardous constituents in the waste within the treatment zone (Section 264.272(c)(2)) is to identify a subset of these hazardous constituents in the waste, labeled principal hazardous constituents (PHCs), that can be used for evaluating land treatment performance. According to 40 CFR Section 264.278, PHCs are defined as "hazardous constituents contained in the wastes to be applied at the unit that are the most difficult to treat, considering the combined effects of degradation, transformation, and immobilization" (40 CFR Section 264.278). PHCs are, by definition, those hazardous constituents having the lowest SSACs, and therefore may be used to indicate the success of treatment in laboratory studies and field verification studies for land treatment demonstrations, and may be used to monitor the long term performance of a full-scale land treatment facility.

PHCs may be identified based on degradation and immobilization estimates using a land treatment mathematical model that is described in Chapter 4 of this guidance manual. The model integrates the combined effects of biological degradation and leaching for predicting levels of constituent(s) in the leachate at breakthrough. The model is useful for selection of PHCs for establishing priorities with respect to constituents that are predicted to be transported the fastest (most difficult to treat) compared with all hazardous constituents identified in the waste.

2.2.7 Use of the SSAC for Design and Management

Through the integration of the combined effects of degradation and immobilization, hazardous constituent movement toward the critical region of the land treatment system, the bottom of the defined treatment zone, can be evaluated. The two primary output parameters of the model used to evaluate treatment are: (1) the concentration of a constituent at the bottom of the treatment zone (defined as "breakthrough"), Cb, and (2) the time required for a constituent to travel a distance equal to the treatment zone (Tb). The ratio Cb/Tb defines the integrated relationship between degradation and immobilization and therefore defines the SSAC. The smaller the ratio, the greater is the SSAC for a hazardous constituent. Constituent-specific degradation and mobility coefficients obtained from various sources (i.e., literature data, theoretical parameter estimation methods, laboratory data, field data, etc.,) for various design and operation and management options given in Table 2.2 can be used in the land treatment model to develop SSAC (Cb/Tb) values for each design/management combination investigated. These SSAC values can then be compared and used to evaluate the following for the LTD:

1. Most appropriate design/management combination for field verification for a specific waste/soil mixture (lowest SSAC values for hazardous constituents).

2. Principal hazardous constituents (PHCs) that will be monitored to ensure effective treatment or to indicate the need for design/management modification of the full-scale operation (set of constituents with the highest SSAC values for the best design/management combination).

After the most appropriate design/management option is selected, based on the results of the ranking described above, PHC selection, degradation, and mobility estimates for hazardous constituents of the waste may be verified through field monitoring activities (Chapter 6) at the full scale treatment site.

2.3 DESIGN AND MANAGEMENT PARAMETERS

2.3.1 Loading Rate

The loading rate (mass/area/application) is the first design parameter that should be determined based on the amount of waste that can safely be applied in a single application. The loading rate is expected to be different for nonacclimated and acclimated soils, and therefore different methods may be used to establish the loading rate depending upon the waste-impacted history of the soil.

Waste application rates (mass/area/application) have been established at many of the land treatment facilities currently operating under interim status permits. For existing facilities operating in compliance with interim status permits, these established rates may be used for the LTD. For facilities following Scenario 3, a method must be used to determine acceptable site-specific application rates for the wastes to be land treated. The use of an appropriate battery of acute toxicity screening tests provides an acceptable method for estimating the initial waste application rates to be used in subsequent LTD studies. However, the final acceptable rate of application must be established by the rate of leaching versus degradation and immobilization in the treatment zone.

This initial loading rate, which may be determined from toxicity screening, therefore should be evaluated in terms of predicted mobility potential based on results of the land treatment model. Site, soil and waste specific data along with predicted and/or measured partition and degradation parameters are used as model input parameters to estimate the fate of hazardous constituents within the treatment zone at the design loading rate(s) evaluated.

2.3.2 Waste Application Frequency

The limit of how much waste may be applied in a single application combined with the frequency of application yields an estimate of the annual waste loading rate (mass/area/yr) feasible at the site. The design initial loading rate(s) can be tested at several frequencies. The test data on degradation rates and mobility for the specific hazardous constituents found in the waste can then be evaluated for determining the SSAC. The timing for waste reapplication may be determined using a soil-based bioassay that indicates detoxification of the waste/soil mixture, or may be based upon a historical predetermined schedule of application of the waste at the initial loading rate(s).

Regardless of the approach used to determine frequency and rate of waste application, effective treatment must be demonstrated, as required in 40 CFR Part 264. This includes demonstration of detoxification (transformation) using bioassay procedures, and demonstration of degradation and immobilization of hazardous constituents in the waste.

2.3.3 Waste Application Method

The selected method of waste application should be demonstrated to result in effective treatment. The SSAC for a particular waste may be a function of the waste application method. If the SSAC established for a given waste and a given soil is unsatisfactory, then modifying the method of waste application may increase the SSAC to an acceptable level. For example, a change in the method of application from surface soil application to waste incorporation on subsurface injection may be effective in increasing the SSAC for waste constituents.

Changing the method of application may also decrease the SSAC for other constituents, however, by limiting soil aeration capacity, etc. Therefore, any modification should be carefully evaluated to determine the overall effect of the method on the SSAC.

If historical operating data suggest that changes to current application methods would not improve waste land treatability, then evaluation of this design option may not be necessary.

2.3.4 Operation and Management Factors

Operation and management factors, addressed in 40 CFR Section 264.272 include those listed in Table 1.2. The effect of these factors on the SSAC may be determined in laboratory and/or field experimental studies. Information from the experiments is used to optimize waste treatment in land treatment facilities in accordance with the standards identified in 40 CFR

Section 264.273. The operation and management factors included in the LTD may be based on current practices, if any, as well as waste/soil/site characteristics which suggest possible improved treatment performance if such management practices are initiated.

Microbial and/or chemical activity may be enhanced through waste/soil incorporation, soil aeration, microbial inoculation, fertilizer application, and establishment of vegetation. If a soil has poor aeration, tilling may be investigated. Fertilizer application should be investigated if soil and waste nutrient levels are low compared with available carbon levels in the waste. Waste/soil incorporation and microbial inoculation may be investigated if indigenous microbial populations are low. Measures for control of soil moisture may include methods for both irrigation and drainage, the evaluation of which would depend upon the water balance at the site, groundwater elevation, concerns for constituent mobility, and soil moisture content required for optimal biodegradation. Soil pH control measures should be investigated if existing soil pH conditions prevent adequate soil microbial activity or produce soil solution conditions that favor inorganic hazardous constituent migration (for example, low soil pH values).

2.3.5 Evaluation of the Effect of Design and Management Parameters on SSAC Values

Information obtained from laboratory studies concerning "volatilization corrected" biodegradation rates, immobilization (partitioning) volatilization rates, initial toxicity, and detoxification rates as a function of loading rates and frequencies, application methods, and operation and maintenance options are used to formulate input to the land treatment model. These input data reflect the combined mobility/degradation effects that allow selection of PHCs for field verification. In addition, the mathematical model provides a tool for:

1. Evaluation of the effects of site characteristics, including soil type, soil horizons, and topography/runon-runoff, on treatment performance;

2. Determination of the effects of design (loading rate, loading frequency), and operation parameters (e.g., irrigation, amendments to increase degradation) on treatment performance;

3. Evaluation of the effects of environmental parameters (e.g., season, precipitation) on treatment performance; and

4. Comparison of the effectiveness of treatment using different design and operating practices in order to maximize treatment.

2.4 FIELD VERIFICATION STUDY

The most appropriate combination(s) of operation and management options, loading rate, and frequency is (are) selected and may be used in a field verification study depending upon the choice of the LTD scenario. The use of laboratory experiments to select options for evaluation in a field verification study may reduce high costs associated with field scale investigations, and may allow for more detailed evaluation of field performances under a limited range of treatment variables.

A short-term (one year) field study should be used to assess the ability of the land treatment unit to prevent hazardous constituents from migrating rapidly out of the treatment zone. Therefore, soil-pore liquid and soil core sampling and analysis for toxicity (toxicity bioassays), soil-pore liquid analyses for mutagenicity potential, and soil-pore liquid and soil core analyses for specific PHCs are considered extremely important to determine migration of hazardous constituents in the field demonstration. Long-term monitoring and continued use of the land treatment model for the land treatment unit during full-scale operation under the Part B permit will allow continued evaluation of treatment effectiveness or for modification to be made in design and management practices to maintain effective treatment.

A one-year field plot study, including waste application and monitoring for treatment effectiveness, is recommended. However, a shorter field verification study (e.g., 6 months) may be conducted if laboratory results indicate rapid treatment of waste constituents. The length of time required for field scale verification may be extended if insufficient data have been obtained, or if waste application or operating practices are not representative of the full-scale facility. Other factors, including unusual weather patterns (e.g., extremely wet or dry season) and inconsistent or contradictory data may be used at the discretion of the permit writer for extension of the time required for the field plot study.

2.5 ANALYTICAL ASPECTS OF CONDUCTING AN LTD

The specific constituents to be measured in wastes, soils, waste/soil mixtures, soil-pore liquid, and groundwater during the performance of an LTD include constituents that may affect the functioning of a land treatment system (Type I analyses), constituents that may affect the performance of other analytical procedures (Type I analyses), and hazardous constituents as defined in Appendix VIII of 40 CFR Part 261 (Type II and Type III analyses). A listing of the three types of analyses, as well as the media to be sampled for each type are presented in Table 2.3.

All procedures used to measure constituents included in Type I analyses should be those approved by the U.S. EPA or should be recognized standard methods. Most of the required methods for these constituents are described in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 (U.S. EPA 1982b), in the Guidance for the Analysis of Refinery Wastes (U.S. EPA 1985a), in Standard Methods for the Examination of Water and Wastewater (APHA 1985), in Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (U.S. EPA 1982a), in Methods of Chemical Analysis of Water and Waste (U.S. EPA 1979), in Methods of Soil Analysis, Part 1: Physical Properties (Black 1965) and in Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties (Page 1982). All analytical data should be reported based on the wet weight of the sample unless otherwise specified. For samples containing water (other than aqueous samples), the percent water should be determined on a representative subsample so that constituent concentrations can be determined on a dry weight basis, if required.

Table 2.3 Suggested Analytical Information for an LTD

Type of Analysis	Purpose	Constituents	Media to be Sampled					
				Soil				
			Waste	Zone of Incorporation	Treatment Zone Below Zone of Incorporation	Below Treatment Zone	Soil-Pore Liquid	Ground-Water
Type I	1. To provide information concerning the land treatability of a waste 2. To optimize other analytical procedures	Water content	X					
		Total residue	X					
		Total volatile residue	X					
		Oil and grease	X	X	X	X		X
		Total organic carbon	X	X	X	X		X
		Extractable hydrocarbons*	X	X	X	X	X	X
		Specific gravity (liquid) or bulk density (solids)	X					
		Total dissolved solids or electrical conductivity (EC)	X	X	X	X	X	X
		pH	X	X	X	X	X	X
		Nutrients (nitrogen, phosphorus, potassium)	X	X				
		Fluoride+	X	X			X	X
		Cyanides+	X	X			X	X
		Sulfides+	X	X			X	X
		Total organic halides‡	X				X	X

Table 2.3 Continued

Type of Analysis	Purpose	Constituents	Media to be Sampled					
				Soil				
			Waste	Zone of Incorporation	Treatment Zone Below Zone of Incorporation	Below Treatment Zone	Soil-Pore Liquid	Ground-Water
Type II	To detect, monitor, and quantify selected Appendix VIII constituents	Appendix VIII metals**	X	X	X	X	X	X
		Appendix VIII organic constituents that are reasonably expected to be in, or derived from waste placed in or on the treatment zone of a land treatment unit	X	X	X	X	X	X
		Principal hazardous constituents (PHCs), which are hazardous constituents contained in the wastes to be applied at the units that are most difficult to treat, considering the combined effects of degradation, transformation, and immobilization (40 CFR 264.278)	X	X	X			

Table 2.3 Continued

Type of Analysis	Purpose	Constituents	Media to be Sampled					
				Soil				
			Waste	Zone of Incorporation	Treatment Zone Below Zone of Incorporation	Below Treatment Zone	Soil-Pore Liquid	Ground-Water
Type III	To identify and quantify Appendix VIII organic constituents	Appendix VIII organic constituents	X	X	X	X	X	X

*If used as an indicator of amount of wastes applied.

+If expected to be present in the waste.

**Total concentrations and not EP toxicity data.

If approved by the permit writer, the hazardous constituents (Type II and Type III analyses) for wastes handled at a facility that are from an identified process (e.g., petroleum refinery processes) for which analysis is required may include only those constituents that are reasonably expected to be in, or derived from waste placed in or on the treatment zone of the land treatment unit (40 CFR 270.20). U.S. EPA has developed such a subset for wastes from petroleum refineries (i.e., the "Skinner List"). The list approved as of October 1985 is included in Table D.1 in Appendix D.

For facilities other than petroleum refineries, guidance for determining constituents for which a facility should test could follow the guidelines given to facilities for preparation of petitions to delist hazardous wastes (U.S. EPA 1985). Two general procedures are given: the facility should submit either (1) a complete listing of raw materials, intermediate products, by-products, and final products; or (2) representative analytical data for all constituents listed in Appendix VIII of Part 261 that are likely to be present in the waste at significant levels, as well as the basis for not analyzing for the other Appendix VIII hazardous constituents. Chapter 6 of the document, Petitions to Delist Hazardous Wastes: A Guidance Manual (U.S. EPA 1985c) should be consulted for a thorough discussion of these approaches. The applicant and permit writer should agree in writing on the specific subset of Appendix VIII constituents at the initiation of negotiations.

Hazardous constituents must be identified and quantified according to procedures and technology approved by the U.S. EPA, i.e., Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 (U.S. EPA 1982b). Additional information on analysis of Appendix VIII constituents may be found in Characterization of Hazardous Waste Sites, A Methods Manual. Volume 3: Available Laboratory Analytical Methods (Plumb 1984).

Methods for analysis of hazardous constituents are complex and require the services of an analytical chemist with experience in hazardous waste analysis. Analytical difficulties often occur when the sample matrix is chemically similar to the analyte, and thus potential interferences may be present in amounts that overwhelm the analytical technique. To deal with severe interferences and yet achieve useful detection limits is a difficult task for the analyst. Interferences may have marked effects on detection limits.

Detection limits of analytes as a function of analytical method, media sampled, and sample size should be calculated and reported. The U.S. EPA has defined detection limit in 40 CFR 136.2(f):

> 'Detection limit' means the minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined by the procedures set forth in Appendix B of this Part.

Regulations outlining this procedure, as well as information on estimating precision, recovery and other quality assurance and quality control considerations may be found in The Federal Register (Vol. 49, No. 209, October 25, 1984, pp. 43234-43442).

At this time, U.S. EPA has not provided definitive guidance on acceptable detection limits for Appendix VIII constituents in different types of environmental samples. The applicant should discuss with the permit writer acceptable detection limits for waste and waste/soil samples. Target detection limits in water samples as reported by a commercial laboratory and by the U.S. EPA are presented in Table E.1 of Appendix E for selected Appendix VIII organic constituents and in Table C.1 of Appendix C for constituents of petroleum refinery wastes. Sample results should be reported for all hazardous constituents as positive values or as below detection limits (BDL).

Clean-up procedures should be used as required to reduce analytical interferences and provide reasonable detection limits. U.S. EPA has developed a document, Guidance for the Analysis of Refinery Wastes (U.S. EPA 1985a) to describe and direct modifications applied to samples from petroleum refining waste streams. Samples containing oil are especially difficult to analyze. Care should be taken not to over-dilute extracts to minimize interferences due to oil, which may result in detection limits which are unacceptable. A possible solution to the problem of analyzing samples containing oil might be to use analytical methodologies that are more sensitive to the constituents of interest (e.g., GC/PID for aromatics and GC/FID for hydrocarbons). Verification of alternative methods should be accomplished by analysis of 5-10 percent of the samples with GC/MS. When reporting results of organic analyses of samples containing oil, the amount of oil present and the cleanup procedures used should be reported. Any modifications made to U.S. EPA-approved standard methods should be documented by the laboratory.

Type II analyses are designed to detect and monitor levels of Appendix VIII volatile and semi-volatile organic constituents on a routine basis using sample extraction preparation techniques and GC and HPLC for detection of organic constituents. These analyses are used for known hazardous constituents such as those listed in an approved subset of Appendix VIII constituents for a specific waste type or those designated as PHCs. The use of Type II analyses allows for the processing of large numbers of samples at lower costs than Type III analyses.

Type II analyses also include the detection of metals in the soil/waste treatment system by the use of ICP or AA. Accumulation of metals are often the factor that controls the total amount of waste that may be treated per unit area. Suggested maximum concentrations of metals that may be safely added to soils (U.S. EPA 1983a) are shown in Table 2.4. The concentrations based on current literature and experience were developed using microbial and plant toxicity limits, animal health considerations, and soil chemistry which reflects the ability of the soil to immobilize the metal elements. Table 2.5 presents suggested acceptable levels of metals for which less data are available (U.S. EPA 1983a). These levels are based on only a limited understanding of the behavior of these metals in soils and should be used as a preliminary guide. If a waste to be land treated contains these metals, laboratory or field tests should be conducted to supplement the limited information in the literature.

Type III analyses are designed to identify and quantify Appendix VIII organic constituents using sample clean-up and extraction techniques and GC/MS

Table 2.4 Summary of Suggested Maximum Metal Accumulations Where Materials Will Be Left in Place at Closure* (U.S. EPA 1983a)

Element	Sewage Sludge Loading Rates+ (mg/kg soil)	Calculated Acceptable Soil Concentrations# (mg/kg soil)	Calculated Acceptable Soil Concentrations# (kg/15 cm-ha)	Soil Concentrations Based on Current Literature and Experience** (mg/kg)
As		500	1100	300
Be		50	110	50
Cd	10	3	7	3
Co		500	1100	200
Cr		1000	2200	1000
Cu	250	250	560	250
Li		250	560	250
Mn		1000	2200	1000
Mo		3	7	5
Ni	100	100	220	100
Pb	1000	1000	2200	1000
Se		3	7	5
V		500	1100	500
Zn	500	500	1100	500

*If materials will be removed at closure and plants will not be used as a part of the operational management plan, metals may be allowed to accumulate above these levels as long as treatability tests show that metals will be immobilized at higher levels and that other treatment processes will not be adversely affected.

+Dowdy et al. (1976); for use only when soil CEC>15 meq/100 g, pH>6.5.

#National Academy of Science and National Academy of Engineering (1972) for 20 years irrigation application.

**If metal tolerant plants will be used to establish a vegetative cover at closure, higher levels may be acceptable if treatability tests support a higher level.

Table 2.5 Suggested Metal Loadings for Metals with Less Well-Defined Information (U.S. EPA 1983a)

Element	Total Loading (kg/ha-30 cm)	Element	Total Loading (kg/ha-30 cm)
Ag	400	Re	4,000
Au	4,000	Rh	2,000
Ba	2,000	Ru	4,000
Bi	2,000	Sb	1,000
Cs	4,000	Sc	2,000
Fr	4,000	Si	4,000
Ge	2,000	Sn	4,000
Hf	4,000	Sr	40
Hg	40	Ta	4,000
Ir	40	Tc	4,000
In	2,000	Te	2,000
La	2,000	Th	2,000
Nb	2,000	Ti	4,000
Os	40	Tl	1,000
Pd	2,000	W	40
Pt	4,000	Y	2,000
Rb	1,000	Zr	4,000

for identification and quantification. These analyses are performed when the identity and levels of hazardous constituents are not known, such as in waste characterization and in degradation studies. They are also used periodically in conjunction with Type II analyses to confirm the accuracy of Type II techniques.

2.6 ANALYTICAL COSTS

With the emphasis on measurement of Appendix VIII constituents in the performance of an LTD, the costs of analytical measurements may be significant. Table 2.6 presents costs estimates for Type I, II, and III analyses. The cost estimates were prepared by Michael Gansecki of U.S. EPA Region VIII after discussion with commercial laboratories. The higher costs quoted are for samples that require more extensive clean-up and extraction/digestion procedures, such as soil samples. Although Type III analyses are more expensive than Type II, they may provide more thorough information on identification of organic constituents than Type II analyses. Because of the potentially high costs of analytical services, careful design is required in developing the LTD plan to obtain the most useful and representative information at a reasonable cost.

Table 2.6 Estimates of Analytical Costs for Type I, II, and III analyses (Gansecki 1986)

Type of Analysis	Cost per Sample
Type I	$20-30/constituent
Type II	
Selected Appendix VIII organic constituents (e.g., HPLC analysis of polynuclear aromatic compounds)	$200-300/sample
Metals	$11-15/metal
Type III	
Appendix VIII organic constituents	
Volatiles by GC/MS	$250-350/sample
Base/neutral fraction by GC/MS	$350-450/sample
Acid fraction by GC/MS	$250-350/sample
Volatiles, base/neutral and acid fraction by GC/MS	$900-1500

CHAPTER 3

PROCEDURES FOR COLLECTING FIELD INFORMATION FOR RECONNAISSANCE SURVEY AND FIELD VERIFICATION STUDIES

3.1 INTRODUCTION

Field information at an HWLT unit may be required for the following reasons:

(1) to determine whether the site/soil/waste system at a new site appears to be appropriate for land treatment;

(2) to identify "uniform areas," and to determine the variation in important soil properties that affect waste treatment within the "uniform areas";

(3) to determine whether there is migration of hazardous constituents from the bottom of the treatment zone at an ISS land treatment unit;

(4) to determine whether groundwater beneath an ISS land treatment unit is contaminated and whether the contamination is due to the land treatment unit;

(5) to evaluate past waste management activities at an ISS unit by means of past waste management records and present waste distribution in the soil;

(6) to identify any "hot spots" in the ISS treatment area, and to determine whether wastes in these "hot spots" are being adequately treated;

(7) to determine the level of accumulation of Appendix VIII metals;

(8) to determine the representativeness of a field verification test area compared to the conditions of the full-scale unit;

(9) to determine the background conditions for the field verification study, including the levels of hazardous constituents in the soil treatment zone; and

(10) to monitor treatment in a field verification study.

Much of this information may already have been gathered to fulfill Part 270 requirements for the Part B application. In particular, an in-depth soil characterization and mapping should have been conducted. Waste analyses should also have been performed to characterize the waste streams (both hazardous and nonhazardous) that will be land treated and used in the land treatment demonstration. For existing units, the reconnaissance information should include chemical characterization of both the waste/soil mixture in the treatment zone of the unit and waste management practices (existing and past) at the land treatment unit.

This chapter summarizes the Part 270 data requirements applicable to treatment demonstration planning and provides additional guidance to the applicant. This discussion supplements the guidance provided in the Permit Applicants Guidance Manual for HWLTSD Facilities (PAGM) (U.S. EPA 1984b), with specifics on how to gather the information suggested by the PAGM. Statistical considerations for the performance of an LTD, including a reconnaissance investigation are presented in Appendix B.

3.2 WASTE CHARACTERIZATION

A demonstration of the land treatability of a waste must first begin with waste characterization. Only after thorough characterization of a waste has been completed can an appropriate LTD be conducted, since comprehensive waste analyses are required to identify and quantify the hazardous constituents in the waste. If significant concentrations of hazardous constituents other than those for which the waste was listed are present, analytical measurements used in the LTD should be more extensive (i.e., analyses for many of the 40 CFR 261, Appendix VIII compounds vs. parameters such as total oil and grease). The converse may also be true: thorough characterization may allow for the elimination of certain analytical procedures during the performance of the LTD. Waste characterization will also provide a preliminary assessment of whether special requirements exist (e.g., site life of the land treatment unit may be determined by total allowable accumulation of metals).

The general Part B information requirements specified under Part 270.14(b) require the submittal of 1) chemical and physical analyses on the hazardous wastes that will be handled at the facility, including all data required to properly treat, store, or dispose of wastes in accordance with Part 264, and 2) a copy of the waste analysis plan. In addition, the specific information requirements under Section 270.20(b) (4) require that an owner/operator of any facility that includes a land treatment unit submits "a list of hazardous constituents reasonably expected to be in, or derived from, the wastes to be land treated, based on waste analyses performed pursuant to Part 264.13." Part 270.20 (a) also stipulates that the description of the treatment demonstration plan must also include a list of potential hazardous constituents in the waste.

The program of routine, broad scale waste characterization conducted for the Part B application only partially fulfills LTD data needs. For the LTD, representative waste batches must be obtained and characterized in detail, especially if an experimental (i.e., laboratory or field verification) demonstration is planned. If the waste for the LTD can be obtained at the time of sampling for general waste characterization, one set of analyses may serve both purposes.

Although an LTD is not required for land treatment of a nonhazardous waste, its presence within the same treatment zone may affect the treatment of the hazardous waste, and vice versa. When nonhazardous wastes are treated in the same treatment zone as hazardous wastes, a detailed characterization of the nonhazardous waste (including Appendix VIII hazardous constituents) must also be provided. The applicant does have the option of segregating the hazardous and nonhazardous wastes at the land treatment unit, and therefore avoid characterization of the nonhazardous waste.

The waste characterization phase is also important for identifying possible capacity limiting constituents (CLC) (e.g., metals) and application limiting constituents (ALC). The limiting levels for the CLCs will depend partially on the closure method employed at the HWLT unit. For a thorough discussion of CLCs and ALCs, the applicant should refer to Chapter 7 of Hazardous Waste Land Treatment (U.S. EPA 1983a).

3.2.1 Sampling and Sample Collection

Sampling of waste should be conducted in accordance with good scientific methods to ensure that accurate, representative samples are obtained. Because waste uniformity and variability always present a problem in treatment demonstrations, all samples should be collected using appropriate sampling and compositing procedures. Multi-phase samples should be homogenized before the sample is aliquoted so that the aliquot taken is representative of the total sample. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 (U.S. EPA 1982b) presents general sample collection requirements and statistical considerations for solid waste samples and should be consulted concerning these protocols. Specific amounts needed for analysis and use in the laboratory and field plot studies depend upon the type of treatment demonstration chosen and on whether an existing site is being used for demonstration of treatability of a waste. The applicant should refer to the appropriate sections of this document when estimating amounts of wastes required to perform the respective treatment demonstration approaches.

In some complex waste generating situations (e.g., intermittent waste generation or seasonal variability), sampling may need to be performed over a period of months to produce a representative set of samples. To decrease the analytical burden, the quantity of waste that will be used in the treatment demonstration could in some cases be collected and stored at the time of sampling and used for overall waste characterization. The waste should be representative of the mixture of waste streams that are land applied, if such a mixture is used. If wastes from different sources are applied to different locations, samples of each waste should be analyzed.

All sampling equipment should be thoroughly clean and free of contamination both prior to use and between samples. Storage containers should be similarly free of contamination. While only plastic or Teflon™ may be used for samples intended for inorganic analysis, glass, Teflon™ or stainless steel may be used for samples intended for organic analysis. Zero-headspace containers should be used for samples collected for analysis of volatile waste constituents. Care should be taken that both the samples and storage container materials are not reactive with the waste. If the sample is to be frozen for storage, ample room for expansion must be provided in the sample container.

3.2.2 Sample Handling and Storage

After a sample has been collected, it must be preserved to protect the chemical and physical integrity of the sample prior to analysis. The type of sample preservation required will vary according to the sample type and the parameter to be measured. Appropriate preservation and storage requirements for different analytical methods are described in SW-846 (U.S. EPA 1982b). The applicant should make prior arrangements with the receiving laboratory to ensure sample integrity until the time of analysis. The Guidance for the Analysis of Refinery Wastes (1985a) presents guidelines for sample handling, preservation and holding times for petroleum refinery wastes.

For wastes that will be used in the LTD, samples may be tightly sealed and preserved at 4°C, or frozen when organic constituents are expected to be lost through volatilization. Freezing may cause multi-phase samples to separate, which are then difficult or impossible to homogenize after thawing. Freezing may be accomplished by packaging sealed sample containers in dry ice directly after collection if other refrigeration methods are not immediately available. For wastes collected for the LTD, preservation methods that may bias the LTD results should be avoided. Since storage of large waste volumes for the LTD may present problems in terms of qualitative and quantitative waste integrity, the applicant should strive to minimize storage time.

At some facilities, wastes that will be land treated may be stored for periods of time before being land applied. This pattern of holding could also be followed for the performance of the LTD. For wastes that are being held for use in the LTD, a set of representative constituents and waste properties could be monitored in order to document changes in waste quality.

3.2.3 Analysis of Waste Characteristics

At the reconnaissance level of investigation, the waste characterization should be as thorough as possible, including Types I and III analyses. Since GC/MS analyses (Type III analyses) will most likely be the detection method used for characterization of organic waste constituents, additional library searches for identification of compounds detected in GC/MS analyses, but not included in the EPA-approved subset of Appendix VIII constituents for the particular industry (e.g., the "Skinner List" for the petroleum industry), are recommended and should not add significantly to the cost of the analyses. Another alternative may be to identify the ten most prominent GC/MS peaks in each waste fraction (i.e., volatiles, base neutral semi-volatiles, and acid semi-volatiles) not otherwise identified as part of the EPA-approved subset.

Quality control procedures must be included as an integral part of the analytical scheme so as to provide a means of determining and improving the quality of information presented. (See Chapter 7 of this manual for a discussion of Quality Assurance/Quality Control.)

3.3 WASTE MANAGEMENT RECORDS FOR AN EXISTING SITE

An existing site should provide, as part of its reconnaissance investigation results, information concerning past waste management practices that clearly document the conditions under which hazardous waste was managed at the site. Table 3.1 lists important waste management data and records. These records should include available history of waste application (i.e., application rates, timing, and location) and available history of waste quality (i.e., waste analysis (especially Appendix VIII constituents) and unit process data. These requirements are more comprehensive than those under interim status standards (ISS), and complete information may not be available. Acceptability of partial information is at the discretion of the permit writer.

These data will be used by the permit writer in conjunction with treatment zone soil core and soil- pore liquid monitoring data to determine uniform areas (which are based on waste loading as well as soil properties), to evaluate the performance of present operating and management practices, and to make modifications as required (i.e., changes which can be tested in the LTD and implemented in the operation of the full-scale facility).

3.4 SOIL CHARACTERIZATION

A basic understanding of the potential for degradation, transformation, or immobilization of a waste involves an understanding of the physical, chemical, and biological properties of the land treatment site. Critical to the treatment demonstration is a thorough understanding of the specific soil that will act as the treatment medium for the waste. Therefore, an in-depth study of the site and soil is necessary. Much of the site information (e.g., hydrogeology, topography, climate, and water budget, including precipitation, runoff, runon, evaporation, and infiltration) should already have been determined to fulfill the Part 270 requirements for Part B of the permit application. The site and soil analysis will identify limiting conditions that may restrict the use of the site as an HWLT unit and, at an existing site, will provide an indication of whether waste constituents are building up, are leaching out of the treatment zone, or whether "hot spots" of waste accumulation exist. The analysis will also provide information for selecting field plot sites if field verification studies are required. The major components of interest in the soil system are the variations in physical, chemical, and biological properties of the soil (U.S. EPA 9183a) and the areal and vertical distribution of waste constituents in the soil.

3.4.1 Soil Survey

A soil survey should already have been conducted for the permit application, according to PAGM guidance. Many areas have already been "broadly" surveyed by the U.S. Soil Conservation Service. If such a survey exists for a given site, it may be used as a guide. However, an existing SCS survey, unless done specifically for the site, cannot be used as a substitute for a detailed site-specific survey and sampling program because the scale used to conduct the SCS surveys is too small, analyses are too few, and often

Table 3.1 Useful Waste Management Data and Records.

Category	Item	Specific Information
History of Waste Application	Years in service and annual quantity of waste land treated	Records of measured annual waste quantity (dry weight) treated over the life of the HWLT unit. Include all wastes, both hazardous and nonhazardous, that are managed on the same unit.
	Placement of wastes on land treatment plots	Records of quantity (dry weight), date, and location of each waste application for each land-treated waste over the life of the LT unit.
	Estimated annual quantity of waste land treated	Estimated annual waste quantity (dry weight) treated during the life of the unit.
	Approximate placement of wastes	Approximate quantity (dry weight), timing, and location of each waste application during the life of the unit.
History of Waste Quality	Waste Analyses	Periodic analyses of each land-treated hazardous waste. (Non-hazardous waste analyses are also necessary if these wastes are land treated in same plot as hazardous wastes.) Parameters should include those listed as Type I analyses and Appendix VIII hazardous constituents, as available.
	Unit Processes	History of unit processes employed in the generation and treatment of the land treated wastes (i.e., wastewater treatment) for the entire unit life.

the surveys do not include all the necessary parameters. If an acceptable soil survey by a qualified soil scientist has not been done, a soil scientist should be retained to conduct the soil survey. The characterization of waste distribution in the soils will require an even more detailed, extensive, and carefully controlled sampling program than is required for the soil survey. Guidance for conducting a soil survey is given in the National Soils Handbook (SCS 1983).

3.4.1.1 Conducting the Soil Survey--

In a soil survey, the soil series present at a given site are identified and sampled. Soil series are differentiated on the basis of both physical and chemical characteristics. The number of samples required to adequately identify the soil series present at a site and to characterize the soils should be determined by the soil scientist. Sampling depth will also vary, depending upon the soils present at the site, but should extend at least to 30 cm below the treatment zone. The geological and hydrogeological characteristics of the site should already have been conducted according to guidance given in the Permit Writer's Guidance Manual for the Location of Hazardous Waste Land Treatment Facilities: Criteria for Location Acceptability and Existing Applicable Regulations (U.S. EPA 1985b).

The soil survey information should include:

(1) Soil profile descriptions

(2) Mineralogy

(3) Use and vegetation

    (a) Permeability
    (b) Flood frequency and duration
    (c) Frost action potential

(4) Estimates of erodibility of the soil (used to design erosion control structures)

(5) Depth and texture of surface horizons and subsoils (used to determine if the soil is suitable for contaminant degradation and to design berms and lined runoff retention ponds)

(6) Depths to seasonally high water table and zones, such as fragipans, that may limit vertical water movement.

The soil survey of a proposed or existing site will be used to define the "uniform areas" of the treatment unit as well as identify any potential problem areas such as inclusions of sandy materials with high permeability. A uniform area is defined as an area of the active portion of an HWLT unit composed of soils of the same soil series to which similar wastes are applied at similar rates. If two or more areas are otherwise similar but receive different amounts of similar wastes, the heavier loaded area may be considered representative of the other(s). Two different soil series may be included in a given uniform area if a qualified soil scientist determines that the characteristics that differentiate the particular soil series in question do not affect the success of land treatment of the particular wastes at the site. The soil scientist may also determine that a single soil series may be divided into two or more uniform areas if those soil properties that affect waste treatment vary significantly within the original proposed uniform area. The soil scientist, therefore, should be familiar with those soil properties that affect treatability of different types of wastes or should consult with a person knowledgeable in waste/soil interactions. A list of selected soil properties which are important in waste treatment and may be included in the soil survey is presented in Table 3.2.

Table 3.2 Soil Physical and Chemical Properties To Be Determined in Soil Survey

Soil Physical Properties	Soil Chemical Properties
Soil texture	Cation exchange capacity
Bulk density	Total organic carbon or organic matter content
Available water capacity	Nutrients (in ZOI only)
Porosity (saturated water content)	Electrical conductivity
Saturated hydraulic conductivity	pH
Particle density	Total organic carbon
Soil temperature	Buffering capacity
Aeration status (saturated or unsaturated)	Type of clay

For new units, the soil within the boundaries of the proposed land treatment unit (i.e., within the boundaries defined by the runon/runoff control structures) should be surveyed along with background soils (i.e., untreated soils outside the boundaries). While the same process should be followed for existing units, difficulties are often encountered as the result of waste additions and soil disturbances, which may have significantly altered active area soil properties. If a definable native soil still exists, the soil survey must emphasize deeper sampling and a greater use of test pits to identify the soil series present, their boundaries, and their continuity with background areas. In some cases, no native soil will be present or identifiable. Nevertheless, the soil scientist should conduct a soil survey to identify "uniform areas."

3.4.1.2 Analysis of Soil Samples Obtained--

Soil samples should be characterized for their chemical and physical properties. The values obtained may be used for management of a land treatment unit and in predictive modeling to evaluate treatment. For an in-depth discussion of these properties and their relationship to land treatment, the applicant should refer to Hazardous Waste Land Treatment (U.S. EPA 1983a) and Review of In Place Treatment Techniques for Contaminated Surface Soils, Volume 2: Background Information for In Situ Treatment (Sims et al. 1984). Analytical procedures for these characteristics may not be widely employed by typical water, waste, and sediment laboratories. Such methods are, however, standard soil procedures used by soil laboratories and are recommended for use to ensure reliable results. Complete discussion of these procedures are presented in Methods of Soil Analysis, Part 1: Physical Properties (Black 1965) and Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties (Page 1982).

The number of samples required to characterize the soil may be determined by the soil scientist using the statistical method similar to those in Appendix B. Enough samples should be analyzed initially to determine representative sample variance. If the variance is large, additional samples may need to be analyzed to establish reliable estimates of variability. Mason (1983) and Barth and Mason (1984) present guidance on sample analysis and determination of variance.

3.4.1.2.1 Soil Physical Properties--Soil physical properties are those characteristics, processes, or reactions of a soil caused by physical forces. Measurements of physical properties that should be included in a soil survey are listed in Table 3.2.

3.4.1.2.2 Soil Chemical Properties--Chemical reactions that occur between waste constituents and the soil must be considered in land treatment demonstrations. Large numbers of complex chemical reactions and transformations, including exchange reactions, sorption, precipitation, and complexing, occur in the soil. Understanding the fundamentals of soil chemistry and the soil components that control these reactions makes it possible to predict the fate of a particular waste in the soil. Chemical properties that need to be evaluated are listed in Table 3.2.

3.4.1.2.3 Soil Biological Properties--The soil provides a suitable habitat for a diverse range of organisms that render a waste less hazardous. The types and numbers of decomposer organisms present in a waste-amended soil depend on soil moisture content, oxygen status of the soil, nutrient composition, and soil pH. Organisms important in the decomposition of wastes have diverse enzymatic capabilities and include bacteria, fungi, and actinomycetes. Although enumeration of species and numbers of microbial organisms is not necessary in the characterization of a land treatment site, a recognition of the importance of these organisms and their role in the waste treatment process is critical. Management of the unit should be designed to manipulate environmental factors to enhance the activity of these decomposer organisms. A discussion of soil organisms is given in Introduction to Soil Microbiology (Alexander 1977).

3.4.2 Characterization of Distribution of Hazardous Constituents in Soil (Existing Sites Only)

Characterization of the distribution of hazardous constituents in the soil at an ISS unit may be used to evaluate the performance of the site. The data may be used to determine: (1) if hazardous constituents are present in the groundwater below the treatment zone (see groundwater monitoring); (2) if hazardous constituents have migrated below the treatment zone; and (3) if degradation, immobilization, and/or transformation are occurring within the treatment zone.

3.4.2.1 Soil Core Sampling--

Waste constituents may move slowly through the soil profile for several reasons, such as: (1) lack of sufficient soil moisture to leach the constituents through the system, (2) a natural or artificial layer or horizon of low hydraulics conductivity, or (3) waste constituents that exhibit only low to moderate mobility relative to soil water. Soil core monitoring can identify any one or a combination of these effects. The intent of such monitoring is to demonstrate whether significantly higher concentrations of hazardous constituents are present below the treatment zone than in background soils. The applicant should refer to the guidance on soil sampling procedures and equipment recommended in the *Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units* (U.S. EPA 1984). Soil samples collected for analysis of volatile hazardous constituents should be collected in zero-headspace containers.

Background should be considered for the area just outside the HWLT unit, and not necessarily an undisturbed, pristine area. The background should be representative of the treatment area, except for past waste applications. Samples should represent the conditions of this background area and should not be selected in a biased manner that would lead to unrealistically low or high concentrations of hazardous constituents. If high concentrations of hazardous constituents are found in the background soils, that fact should be reported to the permitting official.

3.4.2.1.1 *Depth of Sampling*--Soil cores should reach a depth of 30 cm below the treatment zone. After samples of the zone of incorporation are taken, that zone should be removed to avoid contamination of lower horizons. A soil core sampler may be used which extends to the base of the treatment zone. To minimize contamination, the center of the soil core may be removed for analysis. The soil cores may be segmented with depth according to visual changes in soil properties (e.g., texture, color, structure). The zone of incorporation should comprise the first sample. All soil core segments should be analyzed separately. As much of each soil core segment should be analyzed as possible, within the limits of the extraction/digestion and analytical procedures, to ensure that waste constituents present will be detected.

Alternate methods of soil sampling through depth may also be used. Each soil core boring may be segmented according to the following scheme: ZOI, ZOI-45 cm, 45-90 cm, 90-150 cm, and 150-180 cm. Another method is to divide the soil core into four segments: ZOI, an upper treatment zone (TR1), a lower treatment zone that extends to the bottom of the 1.5 m treatment zone (TR2), and a below treatment zone that extends to 30 cm below the treatment zone (BTZ). Since the depth of the ZOI may vary from site to site, depending upon soil conditions and operating practices, TR1 and TR2 are each defined as 1/2 of (B-ZOI), where B is the total depth of the treatment zone. Alternatively, intermediate sampling depths (TR1 and TR2) may be chosen to represent distinct soil horizons within the treatment zone, if they are present. Within each zone, samples should be taken consistently at the same depths in each of these two zones throughout the reconnaissance investigation and in the field verification studies. The amount of soil analyzed from each zone should be as large as possible to ensure detection of waste constituents.

3.4.2.1.2 Areal Distribution of Sampling--While the uniform area delineates the domain of each set of soil samples, the location of each sampling point within each soil series is determined randomly (see Appendix B). In addition to the random sampling points, locations which represent "hot spots" within an HWLT unit should also be sampled and should be analyzed separately. These "hot spots" may include the following locations:

(1) toe slope landscape positions, where runoff may have deposited contaminated soil

(2) soils with a hydraulically restrictive lower horizon that may cause lateral movement of soil-pore liquid, with subsequent accumulation at the base of the slope

(3) saturated areas, such as swales or soils with perched water tables

(4) soils below isolated areas of high permeability

(5) areas where greater than planned amounts of waste accumulate, such as waste unloading locations next to roadways

(6) areas where degradation may have been limited due to inadequate nutrients, lack of sufficient soil moisture, or inappropriate pH levels.

The soil scientist should note any unusual soil conditions that may indicate the presence of "hot spots," such as discolorations or the presence of oil through depth. If a "hot spot" is found during a site investigation, more intensive, repeat sampling of the "hot spot" may be required to determine the potential for leaching of hazardous constituents below the treatment zone and to define possible management options to minimize migration. Details on location of sampling sites are discussed in Appendix B and in Mason (1983) and Barth and Mason (1984).

3.4.2.1.3 Number of Samples--A statistical procedure incorporating the estimated variability of the levels of waste constituents at the site is recommended in determining the number of samples required. Such a procedure is described in Appendix B, in Preparation of Soil Sampling Protocol: Techniques and Strategies (Mason 1983), and in Soil Sampling Quality Assurance User's Guide (Barth and Mason 1984). Alternatively, guidance on the number of samples given in the Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units (U.S. EPA 1984b) may be used. However, caution should be used in compositing samples for analysis.

3.4.2.1.4 Analysis of Soil Core Samples--Soil core samples should be characterized for Appendix VIII constituents, or a subset of Appendix VIII constituents that have been approved by the U.S. EPA, using Type II or Type III analyses, depending on the use of the data. These analyses are required to provide information about both organic and inorganic hazardous constituents that may be present at the site and should be monitored throughout the life of the HWLT unit. This analysis is also required to determine whether an ISS unit is meeting treatment performance standards. Analysis of soil core samples is also required during the performance of a field verification study. The hazardous constituents monitored may be those present at the time of waste application or degradation products not originally in the waste. Because analysis of Appendix VIII constituents is not required under interim status standards (40 CFR 265), the application does not usually possess data concerning all possible hazardous constituents. The extent of accumulation of metals in the treatment zone of the soil may be compared with regulatory limits.

Detection limits for waste constituents in the soil should be reported. If oily wastes are present, these detection limits should be reported as a function of oil content of the sample. Sample results should be reported for all hazardous constituents as positive values or below detection limits (BDL).

The following approach should be used for analysis to preserve the integrity of the data:

(1) Each sample increment in each soil core in the active zone should be analyzed separately so that data on "hot spots" and other possible anomalies will not be lost. Compositing should not be used for these samples.

(2) After background samples have been analyzed and show no hazardous organics, or analyses are begun to determine the mean and variance of hazardous constituents in the background samples, active area samples may be analyzed. Concentrations determined should be compared to the background levels.

The permit writer may, at his/her discretion, allow the applicant to analyze the treatment unit samples first. If no hazardous constituents are found in the groundwater and/or below the treatment zone, the background levels may be assumed to be below detection, and the background soils need not be analyzed separately.

3.4.2.1.5 Interpretation of Soil Core Sample Data--A land treatment unit should be designed and operated such that no vertical movement of significant quantities of hazardous constituents occurs below the treatment zone. In the analysis of the data collected, sound statistical principles should be used. The key to valid comparisons between background levels and levels in the treatment zone is the choice of sample size (number of replications) and the use of random sampling. Guidelines for statistical interpretation of data are presented in Appendix B and the Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units (U.S. EPA 1984) and in Preparation of Soil Sampling Protocol: Techniques and Strategies (Mason 1983).

Data on "hot spots" should be carefully evaluated to determine the potential for migration from these areas below the treatment zone.

3.4.2.2 Soil-Pore Liquid Sampling--

Percolating water added to the soil by precipitation, irrigation or waste applications may pass through the treatment zone and rapidly transport mobile waste constituents or degradation products through the unsaturated zone to the groundwater. Soil-pore liquid monitoring is intended to detect these rapid pulses of contaminants that occur immediately after significant additions of liquids. Therefore, the timing (seasonality) of soil-pore liquid sampling is essential to the usefulness of this technique (i.e., scheduled sampling cannot be planned on a pre-set date, but must be coordinated with precipitation, irrigation, etc.). Soil tensiometers or neutron probes may be installed with the soil-pore liquid samplers to indicate when sampling should be conducted. Soil tensiometers or neutron probes also may be used to indicate if sufficient soil moisture is present for sampling. The use of soil-pore liquid samplers may be restricted to HWLT units located in wetter climates.

Since interim status standards require the installation and use of soil-pore liquid sampling equipment, data concerning the quality of soil-pore liquid below the treatment zone may already exist. However, if these data do not include all the constituents of concern for the LTD and for future management and monitoring, an applicant with presently operating soil-pore liquid samplers should begin collecting samples for analysis of Appendix VIII constituents using Type II (metals) and Type III (organic constituents) methodology. For sites without soil-pore liquid samplers or with samplers that are not functioning, the reconnaissance evaluation may be based on soil core and groundwater data only. If soil-pore liquid samplers have been installed but have not been functioning effectively, possible reasons for their failure (e.g., improper installation, mechanical failures, installation in a soil horizon which has a low hydraulic conductivity, such as a fragipan) should be investigated and corrected, perhaps by changing the type of sampler. To provide minimum volumes required for analyses, liquid samples may be composited from two or more samples. The locations of the composited samples should be identified and reported. The samplers should preferably be located near one another. However, if sufficient volumes of sample for required analyses cannot be collected, a possible priority scheme of analysis may be in the order: volatile organics, semi-volatile organics, and other constituents of interest. Other difficulties that may occur with soil-pore liquid sampling equipment include the potential for absorption of hazardous constituents in the samplers, the potential for release of hazardous contaminants from the samplers and pumps, and volatilization of hazardous constituents during the sampling process. The applicant should note that lack of compliance with Part 265 soil-pore liquid monitoring may affect whether the performance of the facility is considered acceptable and may expose the operator to possible enforcement action. The use of several types of soil-pore liquid samplers is recommended to enhance the likelihood of obtaining samples. A more detailed discussion of soil-pore liquid sampling is presented in the Permit Guidance Manual On Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units (U.S. EPA 1984) and in Chapter 6 of this manual.

3.5 GROUNDWATER MONITORING

Groundwater monitoring data can be an essential part of the reconnaissance investigation and may also be used in field verification studies. For some facilities, groundwater monitoring may be the only source of information concerning hazardous constituents in liquids below the treatment zone, if soil-pore liquid samplers are inoperative. New facilities will be required to implement a groundwater monitoring program according to 40 CFR 264 Subpart F. For existing sites, a groundwater monitoring program should have been implemented as specified in 40 CFR Sections 265.90-94. The monitoring system should consist of (40 CFR 265.91): (1) at least one monitoring well installed hydraulically upgradient from the limit of the waste management area, which yields groundwater samples that are representative of background water quality in the uppermost aquifer near the facility and which is not affected by the facility; and (2) at least three monitoring wells installed hydraulically downgradient at the limit of the waste management area, which are located such that they immediately detect any statistically significant amounts of hazardous waste constituents that migrate from the waste management area to the uppermost aquifer.

However, for facilities consisting of several waste management components, i.e., more than one surface impoundment, landfill, or land treatment area, the ISS groundwater monitoring program may not be sufficient for determining if hazardous waste constituents are migrating out of the bottom of the land treatment unit. ISS do not require separate monitoring systems for each waste management component. If hazardous waste constituents are found in the groundwater from a multi-component waste facility, the owner/operator should install separate monitoring wells immediately downgradient from the land treatment unit to determine if it is the source of the hazardous constituents.

Also, ISS do not specifically require that the groundwater analysis plan include all Appendix VIII constituents or those reasonably expected to be in or derived from the wastes (including inorganic analyses). If those constituents have not been analyzed, the owner/operator should arrange for their analysis as part of the reconnaissance investigation, in order to provide information concerning the effectiveness of treatment in the HWLT unit. Similarly for analyses performed for waste characterization, the compounds analyzed may, on the approval of the permit writer, consist of an EPA-approved subset of Appendix VIII constituents (e.g., the "Skinner List" for the petroleum industry) and the additional ten most prevalent peaks of a GC/MS scan for volatiles, base/neutrals, and acid waste fractions. The presence of any oils or oily sheens on water samples should be noted.

Complete Appendix VIII constituent testing may be required if it is established that groundwater contamination exists at the facility. Under Section 270.14(c)(4), the applicant is required to provide in the Part B permit application "a description of any plume of contamination that has entered the groundwater from a regulated unit." This description should identify "the concentration of each Appendix VIII...constituent throughout the plume," or identify the "maximum concentration of each Appendix VIII constituents in the plume." If evidence of contamination is inconclusive, the regulatory agency may require that only an approved subset of Appendix VIII compounds be measured (e.g., the "Skinner List" for petroleum refinery wastes).

3.6 DATA INTERPRETATION AND PRESENTATION

Reconnaissance information concerning the presence or absence of hazardous constituents in groundwater or below the treatment zone will be used by the permit writer and the applicant for developing the LTD plan and for deciding the required comprehensiveness of the laboratory analyses and studies and field verification studies. At new sites, the information will be used to determine the characteristics of the wastes and the site/soil system that will be used at the land treatment unit and the suitability of the site for land treatment.

The applicant should present to EPA the analytical data from the following activities:

(1) waste characterization
(2) past waste management activities (existing sites)
(3) soil survey
(4) waste distribution in soil (existing sites)
(5) soil-pore liquid monitoring (existing sites)
(6) groundwater monitoring (existing sites)

A map of the land treatment unit should be developed, including the location of the background areas, uniform treatment areas, field verification study areas, "hot spots" of hazardous constituents (at existing sites), and sampling locations for groundwater, soil cores, and soil-pore liquids. Data collected for use in modeling of the land treatment system should be presented in summary form, as well as results of the modeling.

At existing sites, to assess past treatment performance, statistical analysis of soil core, soil-pore liquid, and groundwater data should be conducted by comparing the concentrations of hazardous constituents in the soil cores, the soil-pore liquids, and the groundwater below the treatment zone with background levels. A significant difference would indicate unacceptable hazardous constituent mobility unless other circumstances could account for any such differences (e.g., pockets of buried materials not associated with the land treatment operation or land treatment unit built on former waste disposal site).

A summary of possible statistical approaches and use of field information is given in Table 3.3.

The results of statistical interpretation of data will help to provide the basis for a decision on the choice of the appropriate scenario described in Figure 1.1 (Chapter 1). Specifically these data assist the permit writer in deciding whether the design and operation of the site are acceptable.

Table 3.3 Suggested Uses of Field Information

Type of Information	Statistical Approach	Use of Information
Waste analysis	Mean and variance estimates; confidence intervals	Definition of hazardous constituents and constituents that may affect land treatment
Treatment zone soil-core analysis	Mean and variance estimates; confidence intervals Comparison of individual values with background treatment zone soil core samples at similar depths; tolerance limits Comparison of mean values within a uniform area through time; t-test or ANOVA with multiple comparison between means tests	Distribution and accumulation of hazardous organic constituents through depth (degradation immobilization) Accumulation of metals/comparison with regulatory limits Measurement of degradation products (transformation) Definition of all "hot spots" Evaluation of treatment through time
Below treatment zone soil-core analysis	Mean and variance estimates; confidence intervals Comparison of individual values with background below treatment zone samples; tolerance limits Comparison of mean values within a uniform area through time; t-test or ANOVA with multiple comparison between means tests	Assessment of migration of hazardous constituents below the treatment zone (immobilization) Definition of "hot spots" Evaluation of treatment through time
Soil-pore liquid analysis at bottom of treatment zone	Mean and variance estimates; confidence intervals Comparison of individual values with background soil-pore liquid samples at same depth; tolerance limits Comparison of mean values within a uniform area through time; t-test or ANOVA with multiple comparison between means tests	Assessment of migration of hazardous constituents below the treatment zone (immobilization) Definition of "hot spots" Evaluation of treatment through time
Groundwater	Mean and variance estimates; confidence intervals Comparison of individual values with background groundwater samples	Assessment of migration of hazardous constituents below the treatment zone

CHAPTER 4

PREDICTIVE TOOL FOR LAND TREATMENT DEMONSTRATIONS

4.1 INTRODUCTION

Mathematical models can be utilized to provide a rational approach for obtaining, organizing, and evaluating specific information required to conduct an LTD. A relevant model for an LTD can be considered as a tool for integrating data concerning contaminant transformation, immobilization, and degradation for assessing the relative treatment effectiveness of alternative design/ management combinations. The multiple factors involved in determining the success of land treatment are generally complex and make it difficult to evaluate the effect of each factor on the total treatment process without a tool for interrelating these individual factors. A model also can be used to guide the design of specific experiments and the collecion of specific data that directly address 40 CFR Part 264. Specifically, the effects of design and operating alternatives on the SSAC may be predicted, and the influence of waste type and soil type on treatment may be assessed prior to verification in field or laboratory studies.

A mathematical description of the land treatment system provides a unifying framework for the evaluation of laboratory screening and field data that is useful for the selection of PHCs and for determination of the SSAC for a waste. While current models cannot be relied upon for long-term predictions of absolute contaminant concentrations due to the lack of an understanding of the biological, physical, and chemical complexity of the soil/waste environment, they represent a powerful tool for ranking design, operation, and maintenance alternatives for an LTD as well as for the design of performance monitoring programs.

A mathematical description of land treatment systems, based upon a conceptual model of land treatment that incorporates specific requirements of 40 CFR Part 264.272 as specified in 264.271 and 264.273, provides a framework for:

(1) Evaluation of literature and/or experimental data for the selection of PHCs;

(2) Evaluation of the effects of site characteristics on treatment performance (soil type, soil horizons, soil permeability);

(3) Determination of the effects of design and operating parameters (loading rate, loading frequency, irrigation, amendments to increase degradation), on treatment performance;

(4) Evaluation of the effects of environmental parameters (season, precipitation) on treatment performance; and

(5) Comparison of the effectiveness of treatment using different design and operating practices in order to maximize treatment.

4.2 MODEL DESCRIPTION

The effectiveness of a site for land treatment will depend on its ability to immobilize and/or degrade hazardous waste constituents. There are many mechanisms influencing these two phenomena, and although certain characteristics can be identified and quantified independently for specific substances, it is necessary to express the mechanisms in mathematical terms to evaluate the overall performance of an LTD. The mathematical formulation also facilitates the transfer of knowledge optained at one site to other similar sites.

Short (1985) presented a model (the Regulatory and Investigative Treatment Zone model; RITZ) for use in banning specific hazardous wastes from land treatment. The model is based on the approach by Jury (1983) for simulating the fate of pesticides in soils. The RITZ model has been expanded at Utah State University for this manual to incorporate features which increase its utility for the planning and evaluation of LTDs.

The extended version of the model is programmed for the computer in such a way that additional enhancements (such as unsteady flow and time variable decay transport/partition coefficients) may be incorporated into the model in the future with a minimum of reprogramming. A detailed description of the model equations and a FORTRAN listing of the source code are included in Appendices C&F.Summary description of the model is provided below.

4.2.1 Definition of Terms

There is no terminology which has been universally accepted for describing soil environments used for land treatment of hazardous wastes. Consequently, several important terms are defined here and used consistently throughout the remainder of the discussion.

"Constituent" is the term used for the hazardous substance being tracked by the model. It is a substance exhibiting (or which can be assumed to exhibit) homogeneous chemical properties, i.e., its environmental characteristics may be quantified by a specific isotherm, degradation rate, etc. The constituent may be a pure compound or it may be a mixture of several compounds as long as their behavior can be adequately described by composite constituent parameters.

A "phase" is a physical component of the soil environment. In this application of the model, the following phases are defined: soil grains, pore water, pore oil, and pore air (unsaturated pore space). The relative amounts of the phases may change with time and depth in the soil. The constituent resides in (on) the phases, and the sum of the constituent masses in all phases equals the total mass of the constituent at any particular time.

The constituent may exist in several "states" within the soil environment or even within a phase. The principal state of a constituent will normally depend on the type of phase in which (or on which) it resides. For example, it may be dissolved in the water phase or adsorbed on the soil grains. The constituent will tend to shift from one state to another at some rate of transition until equilibrium is reached.

4.2.2 Model Construct

The model describes a soil column 1 meter square with depth specified by the user (usually 1.5 m). The column consists of a plow zone (Zone of Incorporation, ZOI) and a Lower Treatment Zone (LTZ) as shown in Figure 4.1. The soil environment within the column is made up of four phases: soil grains, pore water, pore air, and pore oil. It is important that all phases and constituent states be included in order to accurately simulate interactions and maintain a mass balance in the model. Characteristics of the soil environment may change with depth and/or time. The waste is applied to the plow zone at loading rates and frequencies specified by the user.

The constituent is acted on by the transport and degradation mechanisms in the model, and its "life history" is calculated at intervals determined by the user. The constituent may migrate from one phase to another during the course of the model simulation. Breakthrough occurs when a pre-determined concentration level is exceeded at the bottom of the lower treatment zone. The average Soil Retention Time (SRT) and Treatment Efficiency are estimated from the model results.

4.2.3 Immobilization/Transport

Once applied to the land and mixed into the plow zone, a constituent may be mobilized by three mechanisms: migration between/among phases, dispersion, and advection.

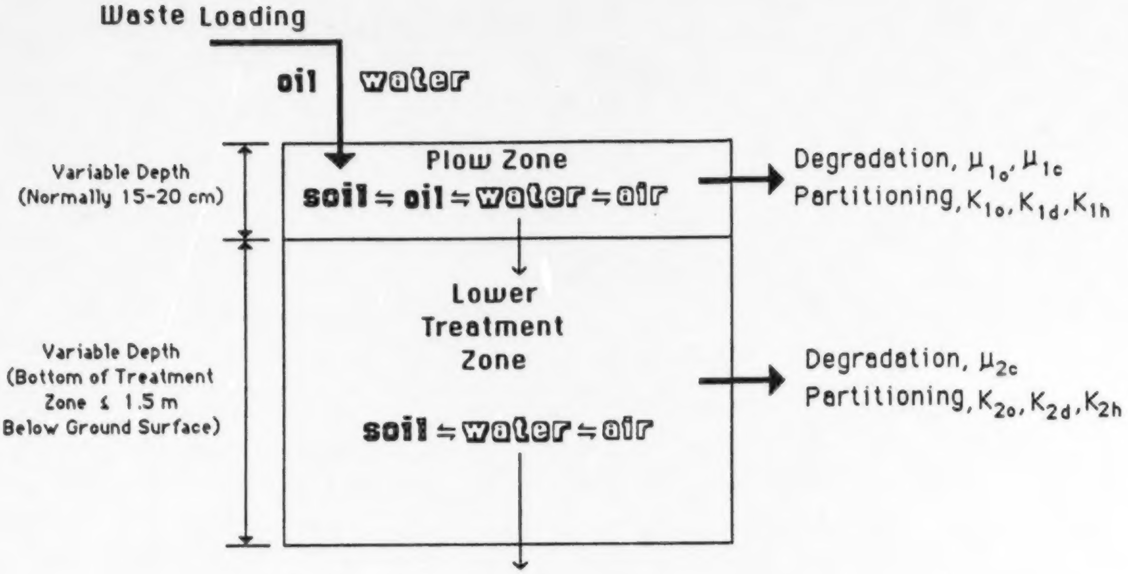
4.2.3.1 Migration--

When two or more phases are in contact, the constituent will tend to migrate between/among them. This mechanism is modeled by assuming that constituent concentrations reach equilibrium immediately between/among all phases which are in contact. This equilibrium condition is described by partition coefficients determined from literature data, laboratory experiments, field sampling, and/or appropriate parameter estimation methods.

Figure 4.2 depicts this relationship in the soil column. The plow zone contains all four phases and the constituents migrate among them to maintain equilibrium. In addition, the oil phase is assumed to decay with first-order kinetics and releases its contents to the other three phases. It is assumed that the oil phase does not penetrate significantly into the lower treatment zone, as indicated in Figure 4.2.

4.2.3.2 Dispersion--

Concentration gradients drive transport within a phase from regions of high concentration to regions of low concentration. Dispersive transport is caused by molecular diffusion and turbulence within the phase. In the


Waste Loading
oil
water
Plow Zone
soil ⇋ oil ⇋ water ⇋ air
Variable Depth
(Normally 15-20 cm)
Degradation, μ_{1o}, μ_{1c}
Partitioning, K_{1o}, K_{1d}, K_{1h}
Lower
Treatment
Zone
soil ⇋ water ⇋ air
Variable Depth
(Bottom of Treatment
Zone ≤ 1.5 m
Below Ground Surface)
Degradation, μ_{2c}
Partitioning, K_{2o}, K_{2d}, K_{2h}

Model Assumptions:
- Periodic Application of Waste
- Oil is Completely Mixed in Plow Zone
- Plug Flow of Water in Plow Zone and Treatment Zone
- Dispersion of Constituent in Unsaturated Pore Space in Plow Zone and Treatment Zone
- Soil Pore Velocity f(site infiltration rate, soil type)

Figure 4.1. Conceptual description of land treatment system used in extended RITZ model formulation.

Fate of Constituent(s):

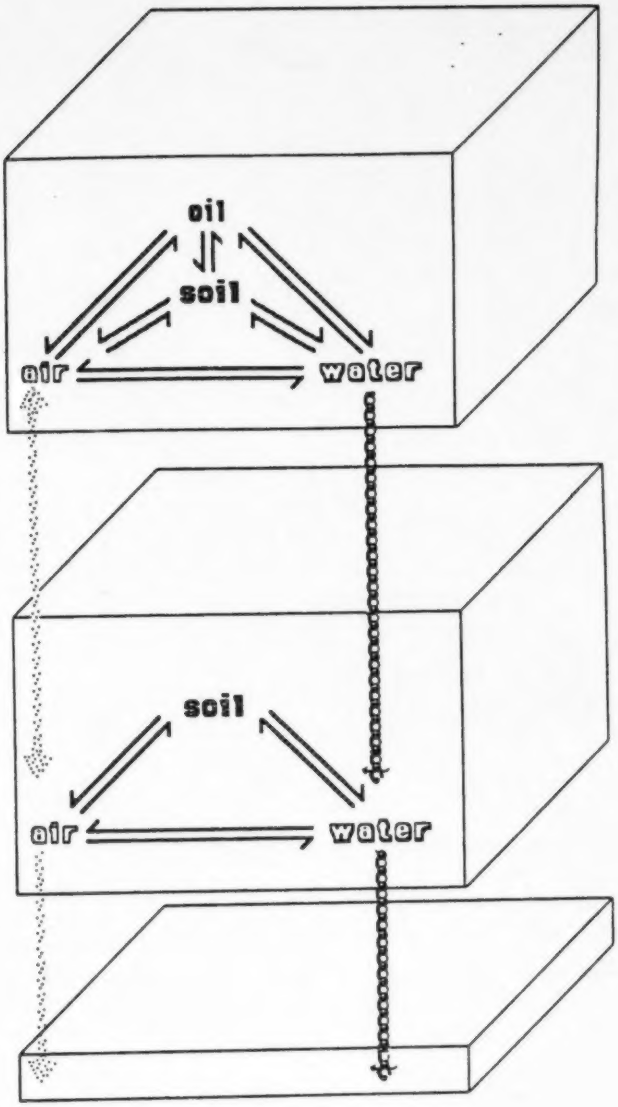
1. Decay
2. Leached when in water moving past bottom of Treatment Zone

Action within Control Volume:

1. Decay of Constituent in all Phases
2. Transfer of Constituent among Phases until Equilibrium reached

PLOW ZONE

LOWER TREATMENT ZONE



Action between Control Volumes:

1. Downward movement of Constituent with Water
2. Upward and Downward movement of Constituent in pore space driven by concentration gradient and properties of Constituent

Figure 4.2. Transport and partitioning relationships within soil control volumes used in modified RITZ model.

model, dispersion is the primary transport mechanism for the volatile fraction of the constituent in the air phase. This mechanism is included in the model because of its importance in distributing the mass of the constituent in the vapor phase throughout the soil column.

4.2.3.3 Advection--

If a phase moves through the soil column, it will transport the constituent along with it. In the model, the water phase and its dissolved constituents are advected at the average soil pore water velocity. This velocity is calculated from the site infiltration rate and the site soil type.

The movement of the constituent is retarded via adsorption/desorption by the other phases that it comes in contact with as it passes through the soil column.

4.2.4 Constituent Degradation

The constituent may be decomposed by biochemical processes which are represented in the model by first-order rate kinetics. Different rate coefficient values may be assigned to different phases and to different depths within the soil column.

4.2.5 Input

Table 4.1 indicates the design/operation information that is used for input to the model. Table 4.2 shows specific input parameters characterizing the waste constituents. These parameters may be obtained from laboratory experiments, literature data, and/or parameter estimation techniques used in conjunction with field and laboratory observations.

4.2.6 Output

The user may select the level of detail for the output of the model results. The output may include the constituent concentrations in each phase at selected depths in the soil column, and at times specified by the user. Output also includes the time to breakthrough of the constituent at the bottom of the designated treatment zone at leachate concentrations at or above constituent detection limits.

Figure 4.3 demonstrates the type of output information that can be obtained from the model. Initially (t = 0), the waste is applied and plowed into the zone of incorporation (ZOI) as depicted in Figure 4.3(a). The concentration of the constituent in the water phase is shown to the right of the figure. The advective velocity of the water is indicated by the downward movement of the shaded areas in Figure 4.3(b),(c) and (d). The movement of the constituent(s) is retarded via adsorption/desorption by other phases as shown by the concentration distributions in these figures that indicate peak concentrations remaining in the vicinity of the ZOI. Figure 4.3(d) shows the condition when the advected water phase reaches the bottom of the treatment zone. Breakthrough may occur at this time if a detectable concentration of the constituent(s) is present in the water phase. Breakthrough may occur at a later time if the constituent is sufficiently mobilized but not degraded during its movement through the upper soil column.

Table 4.1 Design/Operational Variables Required for Use in the Extended RITZ Model

Soil Properties

- soil texture
- saturated water content of the soil
- saturated hydraulic conductivity of the soil
- soil bulk density
- soil organic carbon fraction
- soil particle density
- soil particle effective size

Waste Properties

- concentration of constituent(s) in the applied waste
- mass fraction of oil in the applied waste
- mass fraction of water in the applied waste
- density of oil
- viscosity of oil
- detection limit in aqueous medium of constituent(s) in waste

Environmental Properties

- site recharge rate on monthly or seasonal basis
- site temperature on monthly or seasonal basis

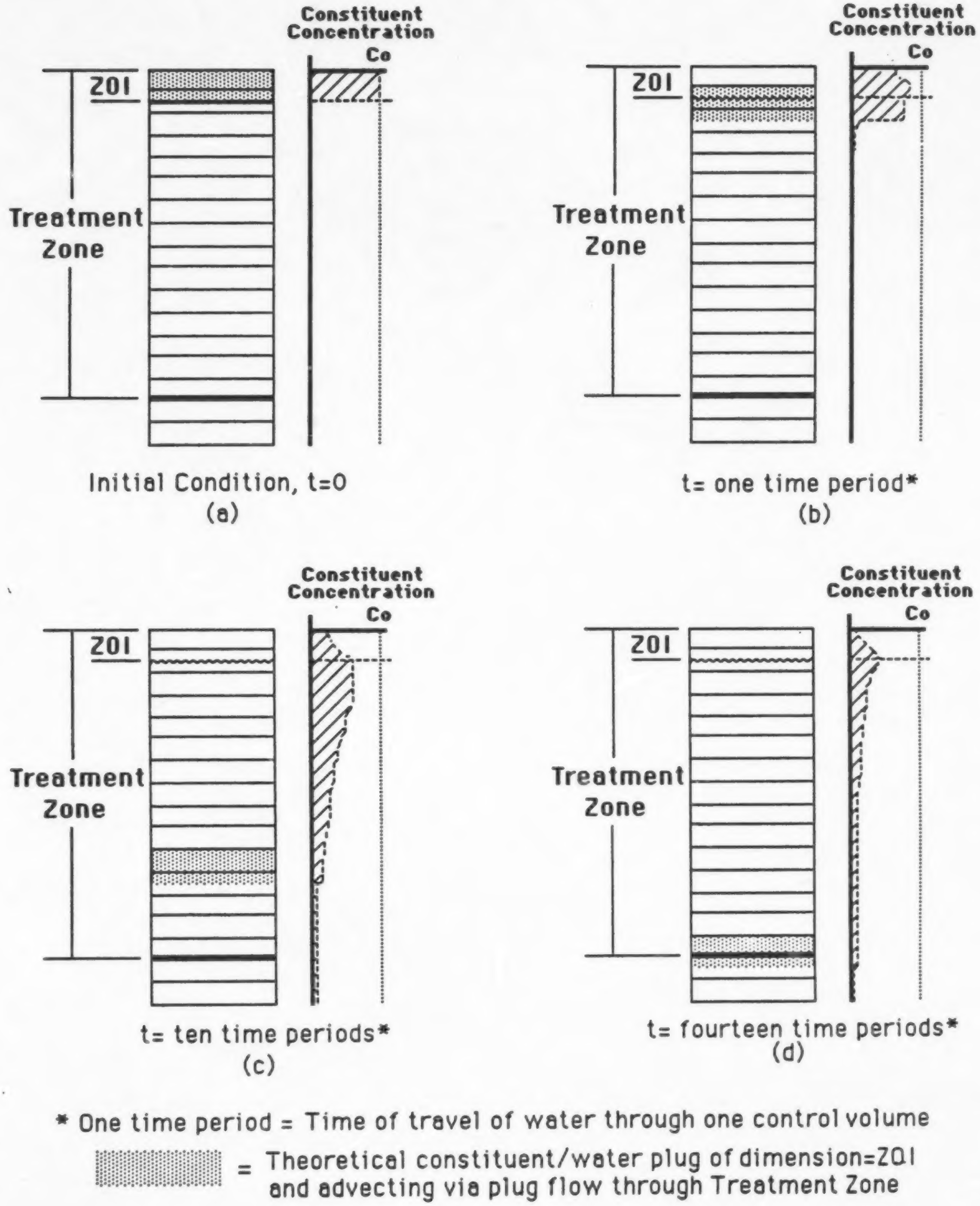
Operational Factors

- plow zone depth (zone of incorporation: ZOI)
- treatment zone depth
- application rate of the waste
- application frequency of the waste
- tilling frequency of ZOI

Table 4.2 Variables Required from Laboratory Analyses, Prediction Methods, Etc., for Use in the Extended RITZ Model

Biodegradation information (for each soil zone as appropriate):
- Half-life ($t_{1/2}$) for each constituent of concern, corrected for volatilization
- Half-life ($t_{1/2}$) of oil in the applied waste;

Immobilization information (for each soil zone as appropriate):
- Ko = partitioning of constituents between water and oil phases
- Kd = partitioning of constituents between water and soil phases
- Kh = partitioning of constituents between water and air phases


Constituent Concentration
Co
ZOI
Treatment Zone

Initial Condition, t=0
(a)

t= one time period*
(b)

t= ten time periods*
(c)

t= fourteen time periods*
(d)

* One time period = Time of travel of water through one control volume

▨ = Theoretical constituent/water plug of dimension=ZOI and advecting via plug flow through Treatment Zone

Figure 4.3. Sample constituent total soil concentration profile at selected time periods after initial waste application.

4.3 MODEL APPLICATION

The results of the model, representing an integration of laboratory, literature, and/or calculated input data, are described for each design/management combination selected for field evaluation. The model outputs for each of the design/management combinations include:

1. Maximum residence time of each constituent in the zone of incorporation (ZOI);

2. Maximum residence time of constituent in the treatment zone;

3. Treatment zone breakthrough time, Tb, for constituent concentration at or above the detection limit if available;

4. Concentration of the constituent in the leachate at breakthrough, Cb, $\geq$ detection limit if available;

5. Retardation factor in the lower treatment zone, below the ZOI; and

6. Velocity of the pollutant in the lower treatment zone, below the ZOI.

Two output parameters are used for making decisions concerning treatment, as described previously. The parameters include: 1) the concentration of a constituent at the bottom of the treatment zone, Cb, $\geq$ detection limit if available, and 2) the time required for a constituent to travel a distance equal to the treatment zone depth, Tb. The ratio Cb/Tb defines the integrated relationship between degradation and leaching (immobilization). The smaller the ratio, the more "successful" is the assessed treatment of a constituent. This simple ratio can be used to evaluate and rank the factors identified above with regard to principal hazardous constituents (PHCs), design/management options, and the effects of environmental parameter changes on treatment as indicated by this Cb/Tb ratio.

PHCs, as defined in Part 264.278, are hazardous constituents contained in the applied wastes that are the most difficult to treat, considering the combined effects of degradation, transformation, and immobilization. The model integrates the combined effects of treatment, as discussed above, for predicting times and concentrations at "breakthrough." For selection of PHCs, the model is useful, not in terms of quantitative determinations of constituent concentrations in the leachate, but rather for establishing priorities with respect to constituents that are predicted to be transported the fastest compared to all other hazardous constituents identified in the applied waste.

The model output, summarized as Cb/Tb for each constituent for each combination of design/management and environmental characteristics, can then be used to select one or more optimum design/management combination(s) to be evaluated in a field verification study. The monitoring program for the field verification study may be based primarily on the PHCs identified from laboratory, literature, and/or estimated input data used in the extended RITZ model. However, it is suggested as described in Chapter 6 of this manual that for 5-10 percent of field samples taken, a complete analysis for all hazardous constituents be conducted to evaluate the accuracy of the model predictions. This approach will also allow field monitoring of any transformation products not predictable by the model. Using this approach for field verification saves costs, while at the same time allows verification of laboratory data and model description without compromising protection of public health during the LTD.

4.4 EXAMPLES

Examples are illustrated for two types of model applications:

1. The recovery of a hypothetical site receiving one waste application.
2. A land treatment site receiving periodic waste applications.

Examples 1 through 3 fall into the first type and Example 4 falls into the second. Physical properties of the soil columns used for all examples are shown in Table 4.3.

Table 4.4 shows the operating parameters and waste characteristics assumed for the four example runs.

The first three columns in Table 4.5 show the results of the model runs for Examples 1 through 3. None of these compounds significantly penetrate the LTZ in detectable levels. The last column in Table 4.5 shows the results of repeated land application of a waste constituent. In order to yield naphthalene penetration into the LTZ, its decay coefficient in the LTZ was reduced to 1/20 of the value in the plow zone (see Table 4.4). Even then naphthalene only penetrated approximately half way into the LTZ.

The upper portion of Figure 4.4 shows the "saw tooth" distribution of the naphthalene concentration in the plow zone. Concentration peaks occur at each 90-day application event and then decay between events. The lower portion of the figure indicates the approximate concentration distributions within the treatment zone at the times indicated. The penetration and attenuation of the naphthalene peaks in the LTZ are clearly seen in the figure.

Table 4.3 Physical Properties of the Soil Columns Used for Examples 1 Through 4

Depth of treatment zone (m)	1.5
Soil moisture coefficient	4.9
Soil porosity (cc/cc)	0.435
Soil bulk density (cc/cc)	1.4
Temperature in the plow zone (°C)	20 (constant)
Temperature in the lower treatment zone (°C)	20 (constant)
Dispersion coefficient in air	0

Table 4.4 Operating Parameters and Waste Characteristics for Examples 1 Through 4

	Example 1 Phenanthrene	Example 2 Benzo(a)pyrene	Example 3 Naphthalene	Example 4 Naphthalene
Depth of the zone of incorporation (m)	0.15	0.15	0.15	0.15
Waste application rate (g waste/100 g soil)	0	0	0	0.06
Constituent concentration in the waste (ppm)	0	0	0	2,000
Weight fraction oil in the waste (Kg/Kg)	0	0	0	0.40
Weight fraction water in the waste (Kg/Kg)	0	0	0	0.40
Density of oil (g/cc)	0.80	0.80	0.80	0.80
Length of application period within year (days)	0	0	0	366
Application frequency within period (days)	0	0	0	91.3
Infiltration rate (m/day)	0.0024	0.0024	0.0024	0.0012
Initial oil content in the plow zone (m^3/m^3)	0.0125	0.0125	0.0125	0.0
Degradation rate of oil (per day)	0.0231	0.0231	0.0231	0.0231
Initial concentration in water, plow zone (g/m^3)	0	0	0	0
Initial concentration in water, LTZ (g/m^3)	0	0	0	0
Initial concentration in oil, plow zone (g/m^3)	60	42	100	0
Initial concentration in oil, LTZ (g/m^3)	0	0	0	0
Initial concentration in air, plow zone (g/m^3)	0	0	0	0
Initial concentration in air, LTZ (g/m^3)	0	0	0	0
Initial concentration on soil, plow zone (g/m^3)	0	0	0	0
Initial concentration on soil, LTZ (g/m^3)	0	0	0	0
Water to oil partition coefficient, plow zone	23,000	4,037,000	1,349	1,349
Water to oil partition coefficient, LTZ (g/m^3 per g/m^3)	23,000	4,037,000	1,349	1,349
Water to air partition coefficient, plow zone	0.006	0.0	0.017	0.017
Water to air partition coefficient, LTZ (g/m^3 per g/m^3)	0.006	0.0	0.017	0.017
Water to soil partition coefficient, plow zone	0.0575	1.69	0.004	0.004
Water to soil partition coefficient, LTZ (g/m^3 per g/m^3)	0.0575	1.69	0.004	0.004
Constituent decay rate in water, PZ (per day)	0.026	0.0075	0.69	0.345
Constituent decay rate in water, LTZ (per day)	0.026	0.0075	0.69	0.0172

Table 4.4 Continued

	Example 1 Phenanthrene	Example 2 Benzo(a)pyrene	Example 3 Naphthalene	Example 4 Naphthalene
Constituent decay rate in oil, PZ (per day)	0.026	0.0075	0.69	0.345
Constituent decay rate in oil, LTZ (per day)	0.026	0.0075	0.69	0.0172
Constituent decay rate in air, PZ (per day)	0.0	0.0	0.0	0.0
Constituent decay rate in air, LTZ (per day)	0.0	0.0	0.0	0.0
Constituent decay rate on soil, PZ (per day)	0.026	0.0075	0.69	0.345
Constituent decay rate on soil, LTZ (per day)	0.026	0.0075	0.69	0.0172

Table 4.5 Summary of Results from Sample Runs

	Example 1 Phenanthrene	Example 2 Benzo(a)pyrene	Example 3 Naphthalene	Example 4 Naphthalene Applied Four Times per Year
Maximum depth of detectable concentration	0.36 m	plow zone	plow zone	0.84 m
Concentration at maximum depth (g/m^3)	0.0010	plow zone	plow zone	0.0014
Time to maximum depth	65 days	initial	3 days	154 days

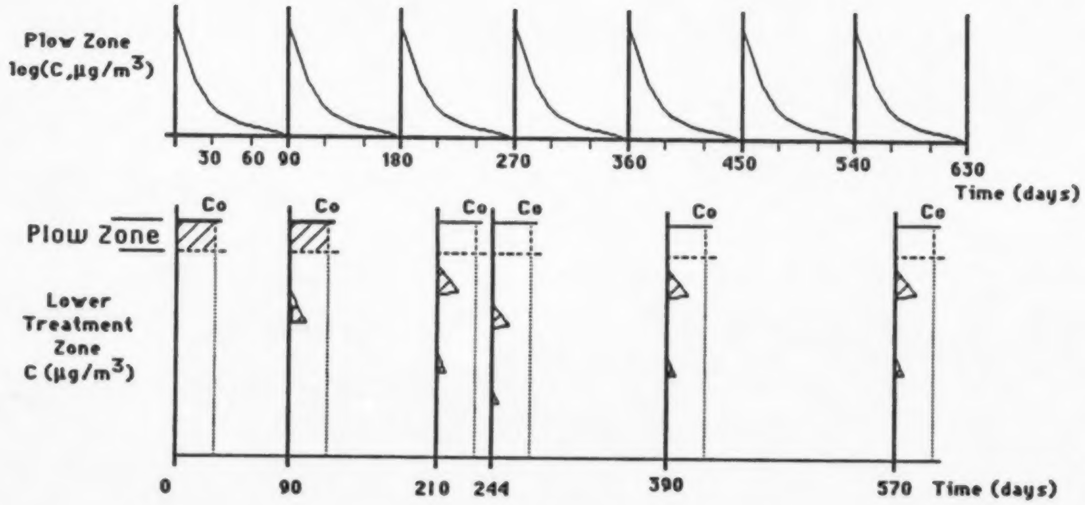


Figure 4.4. Time distributions of naphthalene concentration in the plow zone (upper curves) and depth distributions at specific times in the lower treatment zone (lower curves).

CHAPTER 5

LABORATORY ANALYSES AND STUDIES FOR SELECTING DESIGN AND OPERATION CONDITIONS

5.1 INTRODUCTION

Procedures for measuring degradation, transformation/detoxification, and immobilization, and for organizing, collecting, and processing data are presented in this chapter. Use of data obtained for calculating SSACs and for making decisions concerning treatment effectiveness and design/management options is discussed in Chapters 2 and 4 of this manual.

Evaluation of degradation and immobilization is generally recommended for the zone of incorporation and the lower treatment zone. However, this decision should be based on observed and measured differences between the properties of the zone of incorporation and the lower treatment zone with respect to specific factors that influence waste treatment as identified in Chapter 3 of this manual (Table 3.5).

Analysis of hazardous constituents for determination of degradation and immobilization may be conducted using identification techniques (GC/MS) and monitoring techniques (GC, HPLC, etc.). Identification techniques are recommended for initial and final constituent determinations and confirmation of Appendix VIII constituents (or the subset of Appendix VIII constituents in the waste/soil mixture) in aqueous/soil, aqueous/oil, and aqueous/air phases. Monitoring techniques may be used for obtaining specific data points between initial and final determinations for establishing the mathematical relationships required for calculations of the extent of contaminant degradation and immobilization. Monitoring techniques for determinating data points between initial and final values represents a cost-effective approach for obtaining sufficient information to evaluate design/management options for describing degradation and immobilization of hazardous constituents in the land treatment system.

5.2 WASTE CHARACTERIZATION

The waste characterization performed for the reconnaissance investigation of existing sites may be used for the short-term land treatment demonstration. For new sites, waste characterization should also be conducted according to the guidelines and procedures given for the reconnaissance investigation, as described in Section 3 of this manual. Waste characterization includes analysis of physical and chemical characteristics and constituents of the waste (necessary to optimize other analytical procedures or to provide information concerning the land treatability of the wastes) (Table 3.3) and analysis of Appendix VIII (or an appropriate subset of Appendix VIII) hazardous constituents.

5.3 SOIL CHARACTERIZATION

A thorough characterization of soils present at an existing site should have been conducted for the reconnaissance investigation. At new sites, soil characterization should also be conducted according to the guidelines and procedures given for the reconnaissance investigation, as described in Section 3 of this manual. Information concerning soils may also have been collected as part of initial site investigation of the suitability of the site as a hazardous waste land treatment facility (U.S. EPA 1985). Soil characteristics that should be described and/or measured are discussed in Section 3.5.1 (soil survey information), in Table 3.5 (soil physical and chemical properties), and in Section 3.5.2 (distribution of hazardous waste constituents in the soil).

5.4 TOXICITY OF WASTE TO THE SOIL TREATMENT MEDIUM

Determination of acceptable waste application rates (mass/area/application) is an important step in conducting an LTD. Many land treatment facilities currently operating under interim status may have established acceptable loading rates for their site which may be used for the LTD. However, for interim status facilities with unacceptable loading rates, for newly planned facilities, or for new waste addition to an existing facility, a method to determine initial waste application rates is needed. Since the decomposition of hazardous wastes and detoxification of organic waste constituents in the soil depends to a large extent on biological activities of soil microorganisms, it is important that waste application rates be based on impacts of the waste for indigenous soil microbial populations. These impacts can be measured using a battery of short-term bioassays that measure acute toxicity.

5.4.1 Possible Assays

Appropriate bioassays should reflect the activity and/or survival of the soil microbial population. This information may indicate effects on the microbes responsible for waste degradation. The tests selected should be sensitive enough to indicate adverse impacts of a candidate waste for the soil microbial population, which is directly related to the assimilative capacity of the soil. The objective is to predict initial loading rates that allow detoxification of hazardous constituents to occur within the defined waste treatment soil as a result of normal soil biotransformation processes.

The toxicity screening tests should be easily performed, rapid, and inexpensive. They should also be validated for the ability to demonstrate responses to toxic environments.

Table 5.1 contains a list of suggested toxicity screening bioassays with activities measured and the references for the performance of the bioassays. More detailed descriptions of several of the bioassays, along with procedures, methods, data handling, and interpretation are provided below.

Table 5.1 Toxicity Screening Bioassays Useful in Evaluating Hazardous Waste Applications to Soil

Organism Type	Test Medium	Test	Activity Measured	References
Decomposer	Soil	Viable Counts	Viability	Greaves et al. (1976) Atlas et al. (1978) Greaves et al. (1981)
	Soil	Soil respiration	Organic matter utilization	Atlas et al. (1978) Greaves et al. (1981)
	Soil	Biomass reduction	Growth	Anderson et al. (1981)
	Soil	Organic matter decomposition	Decomposition	Greaves et al. (1976) Malkomes (1980) Porcella (1983)
	Soil	Dehydrogenase activity	Microbial electron transport activity	Atlas et al. (1978) Greaves et al. (1981)
	Soil	Enzyme activities	Biochemical processes	Greaves et al. (1976) Burns (1978) Atlas et al. (1978) Swisher & Carroll (1980)
	Soil	Microcalorimetry	Metabolic heat production	Greaves et al. (1976)
	Soil	ATP or Adenylate charge	Cellular energetics	Atlas & Bartha (1981)
	Soil	Nitrogen cycling processes; fixation mineralization, nitrification, denitrification	Nutrient cycling; specific heterotrophic and autotrophic metabolism	Greaves et al. (1976) Atlas et al. (1978) Greaves et al. (1981)

Table 5.1 Continued

Organism Type	Test Medium	Test	Activity Measured	References
	Soil	Sulfur oxidation	Nutrient cycling; autotrophic metabolism	Atlas et al. (1978)
	Water extract of soil	Microtox™	Bacterial luminescence	Beckman Instruments (1982)
	Solvent extract of soil water	Ames Test	Genetic toxicity	Maron and Ames (1983)
Plant	Soil water extract	Root elongation	Growth	Porcella (1983)
	Soil leachate	*Selenastrum*	Growth	Porcella (1983)
Invertebrate	Soil	Earthworm	Lethality	Neuhauser et al. (1983)
	Soil leachate	Daphnids	Lethality	Porcella (1983)
Vertebrate	Soil leachate	Fathead minnow	Lethality	Porcella (1983)

5.4.1.1 Microtox™--

The Microtox™ system is a simple standardized toxicity test system which utilizes a suspension of marine luminescent bacteria (*Photobacterium phosphoreum*) as bioassay organisms. The system measures acute toxicity in aqueous samples. An instrumental approach is used in which bioassay organisms are handled much like chemical reagents. Suspensions with approximately 1,000,000 bioluminescent organisms in each are "challenged" by addition of serial dilutions of an aqueous sample. A temperature controlled photometric device quantitatively measures the light output in each suspension before and after addition of the sample. A reduction of light output reflects physiological inhibition, thereby indicating the presence of toxic constituents in the sample.

For purposes of the LTD, acute toxicity tests are conducted using the water soluble fraction (WSF) extracted from appropriate samples of waste, soil and/or a series of waste-soil mixtures. An EC50 (effective concentration causing a 50 percent decrease in bacterial bioluminescence) is calculated for each WSF extracted. Results are used to calculate the range of loading rates around a "toxic floor" which will not produce an unfavorable impact on the soil microbial detoxification potential.

The Microtox™ System (Microbics Corporation, Carlsbad, CA) described in this chapter has been evaluated using a large number of pure compounds and complex industrial wastewaters and sludges. This procedure, as with any other toxicity screening test which might be used, offers potential advantages and disadvantages.

The small volume of sample required (as little as 10 ml) and the rapidity in which results can be obtained (less than one hour for the assay itself) are highly desirable features of a screening procedure. It is also reported effective in determining relative acute toxicity of complex effluents containing toxic organic constituents (Qureshi et al. 1982, Vasseur et al. 1984, Burks et al. 1982; Casseri et al. 1983; and Indorato et al. 1984). In each of these studies, Microtox™ results were compared with those from several other assays and were found to provide a reliable indication of the presence of toxic organics. Both Qureshi et al. and Vasseur et al. reported Microtox™ to be more sensitive to complex organic effluents than the other assays tested. King (1984) reported that the production of light by the luminescent bacteria in the Microtox™ reagent is very sensitive to the presence of inhibitory chemicals.

Strosher (1984) reported the assay to be a viable method of screening for apparent toxicity in complex waste drilling fluids. Microtox™ results were found to correlate closely with those from rainbow trout bioassays. Strosher recommended that this assay be utilized as a tool in evaluating effects of drilling fluids on soils. In an earlier paper, Strosher et al. (1980) reported that small changes in concentrations of toxic components could be detected using the Microtox™ procedure. Matthews and Bulich (1985) and Matthews and Hastings (1985) presented results from toxicity screening and toxicity reduction tests conducted using the WSF extracted from different types of waste-soil mixtures.

There are two potential disadvantages to consider. First, the Microtox™ test organism is a photoluminescent bacterium of marine origin, which may not accurately represent the response of soil microbes. In addition, the test procedure is designed to measure the toxicity of water soluble constituents and may underestimate the toxicity of hydrophobic compounds. Reported results from developmental work and evaluation involving different types of waste-soil mixtures tend to discount either disadvantage as a severe hindrance for using the test for general screening purposes (Matthews 1983; Matthews and Bulich 1984; Sims 1985; and Matthews and Hastings 1985). Microtox™ toxicity screening test results have been used by these researchers to establish a range of initial waste application rates that did not result in undesirable impacts on the soil system with respect to treatment potential, thereby allowing detoxification of hazardous organic constituents to occur.

King (1984) reported Microtox™ to be more sensitive to inhibitory chemicals than activated sludge organisms. Slattery (1984) found that when the influent EC50 for Microtox™ became less than 10 percent, activated sludge organisms became completely inactive. The Microtox™ test can be useful for predicting initial waste application rates if a similar relationship exists between the inhibition of Microtox™ bioluminescence and soil microbial activity can be further substantiated.

5.4.1.1.1 Experimental Apparatus--Two major pieces of experimental apparatus are needed to conduct the toxicity screening test procedure as described in this section. A tumbler, wrist-action or platform shaker is used to extract the WSF from each sample. Following extraction, the Microtox™ system is used to determine the relative residual acute toxicity in each WSF sample.

5.4.1.1.2 Water Soluble Fraction Extraction Procedure--A distilled, deionized water (DDW) extraction procedure as described by Matthews and Hastings (1985) is used to generate WSF samples. The following steps are used to prepare these samples for toxicity testing:

a. Place a 100 g sample of each of the background soil, waste, and selected soil-waste mixtures into an extraction vessel, i.e., 500 ml glass flask or bottle. If the waste has a high water content, a thoroughly mixed sample can be centrifuged to obtain the WSF for toxicity testing, thus eliminating the need for the extraction step.

b. Add 400 ml of DDW (4:1 vol/wt extraction ratio) to each vessel and seal tightly.

c. Use a tumbler shaker for mixing. If a wrist-action shaker is used, place the vessels on the shaker at a 180° angle; if a platform shaker is used, place the vessels on their side. In all cases, the extraction vessels must be sealed tightly.

d. Allow the extraction vessels to shake for 20 ± 4 hrs at approximately 30 rpm in the tumbler shaker or 60 rpm on the wrist-action or platform shaker.

e. Following the specified mixing period, remove flasks from the shaker and allow them to sit for 30 minutes. Decant the supernatants into high-speed centrifuge tubes. Add 0.4 g of NaCl for each 20 ml of sample; shake; then centrifuge at 2,500 rpm for 10 minutes.

f. Prepare a sample from each test unit for Microtox™ testing by pipetting 20 ml of elutriate from each centrifuge tube into a clean glass container, sealing and storing at 4°C. Take care to ensure that any floating material is not transferred. As soon as all samples are prepared, begin Microtox™ testing; conduct all tests the same day that they are prepared.

g. Follow the test procedure outlined in the Microtox™ System Operation Manual (Beckman Instruments, Inc. 1982).

5.4.1.1.3 Test System Operation--The Microtox™ toxicity analyzer, associated reagents, and detailed operating instructions can be obtained from Microbics Corporation, Carlsbad, CA. The test involves:

(a) Adjusting the instrument to the desired test temperature, i.e., 15°C.

(b) Adding 0.01 ml of rehydrated cell suspension to serial dilutions prepared by mixing the previously extracted WSF samples in appropriate dilution water.

(c) Taking readings of light outputs at time zero and after the desired reaction time, i.e., 5 minutes for most applications.

(d) Using blank readings to correct for time-dependent drift in light output.

(e) Calculating relative acute toxicity (EC50 values along with upper and lower 95 percent confidence limits) for the WSF extract. This involves preparing a log-log plot of concentration versus gamma (the ratio of light loss to light remaining) corrected for effects of lightdrift based on the blank response. The concentration of the sample corresponding to a gamma of 1 is termed the EC50 (t,T), meaning at this concentration a 50 percent decrease in light output occurs for an exposure time (t) and test temperature (T).

5.4.1.2 Soil Respiration--

Soil respiration is generally accepted as a measure of overall soil microbial activity (Hersman and Temple 1979) and has been used as an indicator of the toxicity or of the utilization of organic compounds added to the soil environment (Pramer and Bartha 1972). Respiration may also act as an indicator for microbial biomass in soil because the transformations of the important organic elements (C,N,P, and S) occur through the biomass (Frankenberger and Dick 1983). Measurement of CO_2 evolution from soil samples is a commonly used indicator of soil respiration, although measurement of O_2 uptake using a Warburg-type respirometer is a viable alternative for short-term respiration. Evolution of CO_2 can be measured in flow-through or enclosed systems. Flow-through systems involve passing a stream of CO_2-free air through incubation chambers and then capturing CO_2 from the effluent gas stream in alkali traps (Atlas and Bartha 1972). The Biometer flask described by Bartha and Pramer (1965) is an example of the enclosed system. It consists of an Erlenmeyer flask modified with a side-arm addition which serves as an alkali reservoir for trapping CO_2. A septum in the side-arm allows for removing samples of the alkali. The flask itself is fitted with an ascarite trap for maintenance of CO_2-free aerobic conditions within the container. The carbon dioxide produced by microbial respiration is quantitated by titration of the alkaline solution with an acid of known normality or by determination of total inorganic carbon in the solution through use of a carbon analyzer.

Determination of soil respiration through CO_2 evolution is an inexpensive and simple method for indicating general soil microbial activity and acute effects of added substrates on that activity. The use of soil respiration in the literature is widespread, indicating the general acceptance of respiration as an indicator of soil microbial activity. Soil respiration is limited in that results will not necessarily reflect changes in specific types and/or groups of microorganisms.

5.4.1.2.1 Experimental Apparatus--Each experimental unit consists of a 500 ml Erlenmeyer flask having a single-hole stopper fitted with an ascarite trap. A stiff wire, bent to an 'L' shape at the bottom, is suspended from the stopper. A scintillation vial attached to the wire with a rubber band contains 0.5 N KOH for capturing CO_2 released from the soil.

5.4.1.2.2 Experimental Procedure--The method recommended below is modified from the procedure described by Bartha and Pramer (1965).

a. Distribute 50 g of each of the background soil, waste, and soil: waste mixtures to 500 ml flasks, using triplicates for each loading. Include three empty flasks as blanks and treat blanks in an identical manner to samples throughout the testing period.

b. Place a scintillation vial filled with 15 ml of a 0.5 N solution of KOH into each flask and secure the stoppers.

c. Incubate the flasks at room temperature (22 ± 1°C).

d. Monitor the evolution of CO_2 for a 24-hour period. For determinations of detoxification potential, CO_2 evolution should be monitored at specific time intervals.

e. The alkali traps are changed by removing the vial of KOH from each flask, capping it, and replacing the vial with one freshly filled with alkali.

f. Determine the amount of CO_2 in each trap using a carbon analyzer and testing for total inorganic carbon. Where a carbon analyzer is not available, the amount of CO_2 evolved can be determined titrimetrically. Add an excess of $BaCl_2$ to the alkaline solution to precipitate the carbonate as insoluble $BaCO_3$. With phenolphthalein as an indicator, titrate the unreacted KOH with 0.6 N HCl. Calculate evolved carbon expressed as CO_2-C, using the following formula (Stotzky 1965):

mg CO_2-C = [(ml of HCl to titrate blanks) - (ml of HCl to titrate sample)] x normality of HCl x equivalent weight; equivalent weight = 6 if data expressed in terms of carbon.

g. Subtract the mean amount of CO_2-C found in the blank flasks from the mean of the results from the other flasks. This accounts for the CO_2 which enters the flasks when samples are taken and the flasks are aerated.

h. Check the moisture content of each unit once a week. The availability of water has a large effect on microbial activity.

5.4.1.3 Dehydrogenase Activity--

Dehydrogenation is the general pathway of biological oxidation of organic compounds. Dehydrogenases catalyze the oxidation of substrates which produce electrons able to enter the electron transport system (ETS) of a cell. Measurement of dehydrogenase activity in soils has been recommended as an indicator of general metabolic activity of soil microorganisms (Frankenberger and Dick 1983; Skujins 1973; Casida 1968). Free dehydrogenases in soil are not expected because cofactors such as NAD and NADH are required, linking dehydrogenase activity to living organisms (Skujins 1978). The type and quantity of carbon substrates, both present and introduced, will influence dehydrogenase activity (Ladd 1978; Casida 1977).

The soil dehydrogenase assay involves the incubation of soil with 2,3,5-triphenyltetrazolium chloride (TTC) either with or without added electron-donating substrates. The water-soluble, colorless TTC intercepts the flow of electrons produced by microbial dehydrogenase activity and is reduced to the water-insoluble, red 2,3,5-triphenyltetrazolium formazan (TTC-formazan). The TTC-formazan is extracted from the soil with methanol and quantified colorimetrically.

The soil dehydrogenase activity assay is simple and efficient. It is also a convenient test to run since the only major pieces of equipment required are a spectrophotometer, a centrifuge, and, depending on selected test conditions, an incubator. However, since the assay indicates general activity of the major portion of the soil microbial community, it may not reflect effects of an added substrate or toxicant on specific segments of the community.

5.4.1.3.1 Experimental Apparatus and Procedure--The method for determination of dehydrogenase activity is based on Klein et al. (1971). Activity both with and without glucose addition is determined. Work by Sorensen (1982) found that increased soil dehydrogenase activity due to glucose addition can be more sensitive to stress than the activity without glucose.

Triplicate test units are prepared for each of the background soil, waste, and soil:waste mixtures. Color correction is accomplished by preparing one additional tube for each combination of soil:waste mixture with or without glucose that does not include TTC.

For each sample:

a. Weigh 2 g soil into each of two 16 x 150 mm culture tubes.

b. Add 0.4 ml of a 4 percent (w/v) solution of TTC to each tube.

c. Into one tube add 1 ml deionized water. To the other tube add 1 ml of 0.5 percent glucose.

d. Mix the tubes on a vortex mixer, place stoppers in the tubes, and incubate at 35°C for 22 ± 2 hours.

e. Add 10 ml methanol to each tube. Shake the tubes vigorously for 1 min to extract the TTC-formazan. Allow the tubes to sit overnight, then shake again for 1 min and centrifuge at 600 x g for 10 min.

f. Read the absorbance of the supernatant from each sample at 485 nm using a 1 cm light path with methanol as a blank.

g. Determine dehydrogenase activity from a standard curve derived from TTC-formazan standards of 1, 2, 5, 10, and 20 mg/l in methanol. Calculate color-corrected results by subtracting the absorbance value obtained for each sample having no TTC from corresponding TTC-containing samples. Express results as g formazan produced per gram dry weight of soil in 24 hours.

5.4.1.4 Nitrification--

Oxidation of ammonium-nitrogen to nitrite and then to nitrate nitrogen is called nitrification. The chemoautotrophic bacteria that derive their energy for growth from the oxidation of ammonium ion (e.g., *Nitrosomonas*) or nitrite ion (*Nitrobacter*) are sensitive to environmental stress and are not different from their heterotrophic microbial neighbors in the soil in many of their requirements for metabolic activity and growth (Focht and Verstraete 1977). Coupled with the fact that the energy yielding substrates and/or oxidized products of nitrification are easily extracted from the soil and measured, the process of nitrification can be used as an excellent bioassay of microbial toxicity in the soil. Nitrification is a process which influences soil fertility since the nitrate anion is very mobile in soil and easily leached while the ammonium cation is strongly absorbed. Therefore, information about the nitrification process helps in understanding the status of nitrogen cycling in the soil.

A possible disadvantage of using nitrification as a toxicity indicator is the high sensitivity of the bacteria involved. This is especially true of *Nitrobacter* (Focht and Verstraete 1977). Heterotrophic microbes may be more resistant and resilient and as they are the organisms involved in waste stabilization, this assay may overestimate the general toxicity potential of the waste.

5.4.1.4.1 *Experimental Apparatus and Procedure*--The methods outlined below were used by Sorensen (1982) as adapted from Belser and Mays (1980). The intent of the assay is to measure the potential activity of the ammonium or nitrite oxidizing bacteria in the soil over a relatively short period of time, and not to measure the ability of the soil to support growth of these organisms over an extended period. Substrate concentrations are kept low to avoid toxic effects, and to avoid the necessity of dilution prior to nitrite analysis.

Initial Potential NH_4+ Oxidation Activity Procedure--

For each sample:

a. Weigh 6 g of soil into a 125 ml Erlenmeyer flask.

b. Add 25 ml of ammonium-phosphate buffer solution containing 167 mg K_2HPO_4/l, 3 mg KH_2PO_4/l, and 66 mg $(NH_4)_2SO_4$/l. The pH of this solution should be 8.0 ± 0.2. Note: A buffer close to the test soil pH may be desirable.

c. Add 0.25 ml of 1 M $NaClO_3$ to each flask to block NO_2-oxidation.

d. Cover the flask with aluminum foil and shake on an orbital shaker at 200 rpm for 22 ± 2 h at 24 ± 2°C.

e. Clarify the slurry or a portion of the slurry by centrifugation or filtration.

f. Analyze the filtrate or centrate for NO_2-N (Kenney and Nelson 1982; APHA 1985). Each batch of ammonium-phosphate buffer should also be analyzed for NO_2-N and the concentration subtracted from sample results.

Initial Potential NO_2-Oxidation Activity Procedure--

a. Weigh 6 g of soil into a 125 ml Erlenmeyer flask.

b. Add 25 ml of nitrite-phosphate buffer solution containing 167 mg K_2HPO_4/l, 3 mg KH_2PO_4/l, and 4.5 mg $NaNO_2$/l. The pH of this solution should be 8.0 ± 0.2. Note: A buffer close to the test soil pH may be desirable.

c. Add 5 1 of a 20 percent solution of nitropyrin (2-chloro-6-(trichloromethyl) pyridine) in dimethyl sulfoxide to each flask to block the oxidation of indigenous NH_4^+ to NO_2^- (Shattuck and Alexander 1963).

d. Process each flask and its contents as described for NH_4^+ oxidation described above in Steps d through f. In this case the NO_2-N concentration in the nitrite-phosphate buffer is the initial substrate concentration.

5.4.1.5 Soil Plate Counts--

Total counts of major microbial groups in the soil are intended to show the viability of the soil microbial community. Comparison counts made before and after waste addition provide an indication of acute microbial toxicity to the specific microbial groups and show the effect of waste addition on the community as a whole. Dominant species may be suppressed, allowing for an increase in the predominance of less common groups.

Ideally, the plate count procedures should create optimal conditions for the microorganisms to be enumerated, therefore, medium composition, incubation conditions and length of incubation are important considerations in plate count assays. It is improbable that all types of microorganisms present in the soil will be detected using agar plates, since all media types are selective to a certain extent (Greaves et al. 1976). Another disadvantage of the plate count assay is that comparisons made among enumerations performed at different times will be accurate only if test conditions for each set of counts are identical. In addition, the plate count method is not conducive to counting numbers of filamentous organisms or those producing large quantities of spores. Also, there is not necessarily any correlation between numbers of microorganisms and measured metabolic activities (Greaves et al. 1976). The microbial life forms suggested for enumeration, i.e., total bacteria, actinomycetes and fungi, are the most important soil organisms effecting biological degradation and transformation of hazardous waste constituents.

5.4.1.5.1 Media Preparation--The following three media are recommended for determining viable counts of the selected microbial types: tryptic soy agar for bacteria, Martin's rose bengal media for fungi, and starch-casein agar for actinomycetes. Details on preparation of these media can be found in Wollum (1982).

5.4.1.5.2 Experimental Procedure--

a. Prepare a sufficient quantity of plates of each media type.

b. Prepare dilutions of the control soil and each soil:waste mixture in triplicate according to section 4.2.2 of Wollum (1982). Three dilutions of each replicate are plated on each type of media. For bacteria and actinomycetes 10^{-6}, 10^{-5}, and 10^{-4} dilutions are recommended. For fungi, the suggested dilutions are 10^{-5}, 10^{-4}, and 10^{-3}. The dilutions to be used should encompass the optimum number of organisms for counting, i.e., 30-300 colonies for bacterial and actinomycete plates and 10-20 for fungal plates. All dilutions shoul be prepared in the same manner since comparisons across treatments are to be made.

c. Prepare spread plates according to section 5.2.2 of Wollum (1982).

d. Incubate the plates at a controlled temperature, generally between 24 and 28°C. The period of incubation depends on temperature and growth conditions. For bacteria and fungi, 4 to 7 days should be sufficient, while actinomycete plates may have to be incubated 10 to 14 days for adequate results.

e. Average the number of colonies per plate for each dilution and determine the number of colony-forming units per gram dry weight of soil. Significant differences in numbers of colony-forming units from the control can be determined using statistical tests. A significant reduction in the number of colony-forming units found in the soil treated with waste as compared to control soil indicates the degree of acute toxicity of the complex waste mixture.

5.4.2 Preparation of Waste Soil Mixtures for Bioassays

If air-dried soil is used, it should be brought up to the desired moisture content (minimum 60 percent of the water-holding capacity of the soil, preferably a moisture content that will prove typical for field conditions). The soil is acclimated for 7 to 10 days to allow for proliferation of soil microorganisms. After the acclimation period, waste which has been thoroughly mixed is added to the soil at the previously selected loading rates. When small percent loadings are to be tested, i.e., $\leq$ 10 percent, it may be difficult to evenly disperse the waste material in the soil. The use of an organic solvent as a dispersal agent may not be feasible in all cases since some solvents have toxic effects on microbial processes. The following method (Utah State University 1986) has proved successful for providing a fairly uniform distribution of small quantities of waste in soil. A soil:waste mixture at a concentration much higher than the upper loading rate is prepared using air-dried soil. The waste is incorporated into the soil by mixing on a rotary tumbler for 12 hours at 30 rpm. This soil:waste concentrate can be "diluted" with additional acclimated soil so that the final concentration of waste is equal to the desired loading rate.

After the waste has been added to the soil and thoroughly incorporated, the soil:waste mixture is allowed to incubate 22 ± 2 hours. This incubation allows for acute effects of the waste on soil microbiota to be expressed. After the incubation period, the selected toxicity assays are begun. Except for soil plate counts, the assays described in this chapter require 24 hours for incubation or extraction.

5.4.3 Determination of Loading Rates

5.4.3.1 Preliminary Loading Rate Investigation--

In order to use any of the previously described acute toxicity tests for determining an appropriate range of waste application rates, a set of initial rates to test should be chosen.

5.4.3.1.1 Microtox--Matthews and Hastings (1985) have described a method using the Microtox assay to determine an initial range of waste application rates. The following steps are involved:

a. Obtain a 5 kg sample of the site soil and a 1 kg sample of the waste to be applied. Follow the sample collection procedures referenced in this manual to insure that characteristics of soil and waste samples are representative of those anticipated at the site.

b. Weigh out two 100 g aliquots of air-dried soil which has been crushed and sieved to 2 mm for soil toxicity determinations; weigh out two 100 g aliquots of waste which has been thoroughly mixed.

c. Prepare WSF samples for toxicity testing by extracting aliquots of the duplicate waste and soil samples as described in the Microtox™ methods section.

d. Conduct Microtox™ tests on each WSF sample prepared as previously described. Experience suggests that if the EC50 for the WSF of a given waste as defined by the Microtox™ system exceeds 25 percent, the EC50 for the WSF of any waste-soil combination will exceed 20 percent and toxicity as measured by the Microtox™ system will not be a significant factor in determining loading rate. This does not preclude use of the test system to determine if toxicity reduction of hazardous organic constituents within the waste-soil matrix is occurring over time.

e. If the soil WSF is non-toxic, i.e., the full strength DDW extract effects ≤ 25 percent decrease in bacterial bioluminescence, the soil has no apparent residual toxicity. If soil residual toxicity is indicated (> 25 percent decrease in light output in the full strength DW extract), the cause of this toxicity should be determined prior to further testing.

f. Determine four loading rates to be used in subsequent toxicity screening tests according to the following criteria:

1) Calculate the EC50 and 95 percent confidence limits for the waste WSF.

2) Choose the upper limit of the 95 percent confidence interval as the highest loading rate to be used. For example, if the WSF of the waste has an average EC50 of 10 percent and upper and lower 95 percent confidence limits of 12 percent and 8 percent, the highest loading rate would be 12 g of waste per 100 g of soil.

3) Use 1/4, 1/2, and 3/4 of the upper limit as the remaining three loading rates (in percent wet weight waste per dry weight soil) for testing.

g. Weigh out four 300 g samples of prepared soil. Add prescribed amount of waste and mix thoroughly to achieve the four loading rates (wt/wt) described above. Let the waste:soil mixtures incubate at room temperature ($22 \pm 2°C$) for 22 ± 2 hours before proceeding.

h. From each of the four waste:soil samples, remove three 100 g (dry wt) subsamples and place in a flask or bottle for extraction. Discard the remainder of the sample.

i. Extract each of the 12 subsamples with DDW according to the procedure described in Section 5.2.1 and conduct the Microtox™ test on the WSF constituents.

j. Calculate the EC50 and 95 percent confidence limits for each waste-soil WSF. Average triplicate values to obtain EC50 and 95 percent confidence limits for each loading rate extracted. Transpose each EC50 value to toxicity units (TU) in soil using the following equation:

$$\text{Soil TU} = \frac{100}{\text{EC50}} \times 4$$

k. Prepare a log-log plot of toxicity units versus loading rates for use in estimating an acceptable initial loading rate window. The interception point for 20 soil TUs is the lower loading limit for the window; the upper limit is defined as twice the lower limit. Experimental data generated to date suggest that this is a reasonable window for initial loading.

This procedure was developed based on experience with several classes of hazardous wastes being evaluated for land treatment in experiments conducted at the U.S. EPA Robert S. Kerr Environmental Research Laboratory at Ada, Oklahoma, and the Utah Water Research Laboratory, Utah State University, Logan, Utah.

5.4.3.1.2 Other Assays--When using assays other than Microtox™ for preliminary initial application rate estimation, the following procedure may be useful:

a. Choose three or four loading rates that cover the range from 0 to the maximum rate likely to be used based on mobility, soil hydraulic conductivity effects, anticipated degradation rates, or other criteria. Concentrations used should vary by a factor of 10 (e.g., 0, 0.1, 1, and 10 percent by weight).

b. Perform the selected acute toxicity bioassays on each of the soil: waste mixtures.

c. Beginning at the concentration showing little or no toxicity in step b above, prepare a series of loadings that encompass the concentration where activity is reduced approximately 50 percent relative to the untreated control. Smaller increments in concentration should be used than in step a above.

d. Again, perform the accute toxicity bioassays. The results of these assays should identify a range of loading rates that are not highly toxic to the soil biota, and that can be used in laboratory detoxification studies.

5.4.3.2 Selecting Waste Loading Rates--

Giving greater weight to the level of toxicity indicated by assays which indicate activity among a broader spectrum of the microbial population (e.g., respiration and dehydrogenase) or indicating general toxicity (Microtox™), but considering all assay results, select a range of loading rates which is not likely to inhibit decomposition but will use the apparent assimilative capacity of the soil.

5.4.4 Data Interpretation

No single assay is likely to indicate the activity or viability of the broad spectrum of soil microorganisms or their functions. Measurements of respiration may represent the activity of the broadest community of microorganisms, but high rates of respiration by organisms with narrow metabolic capabilities, when appropriate growth substrate is available, may mask the reduction in activity of a larger spectrum of organisms. When information on the toxicity of a waste or its degradation or transformation products is available from more than one assay, decisions on acceptable levels of toxicity for loading rate determinations or determination of detoxification will be more reliable. Broad spectrum assays (e.g., respiration or dehydrogenase) and general toxicity (Microtox™) are recommended, but assays relating to specific subgroups of the microbial community (e.g., nitrification, nitrogen fixation, or cellulose decomposition) may also be considered.

Assays measuring universal metabolic activities (e.g., carbon dioxide evolution) or general toxicity (e.g., Microtox™) may be weighted highest in decision making, but if other assays indicate severe toxicity, lower loading rates should be investigated.

5.5 TRANSFORMATION/DETOXIFICATION OF THE WASTE:SOIL MIXTURE

Transformation/detoxification data are used to evaluate rates of detoxification relative to the mobility of PHCs in the soil. Compounds with high mobility in the soil must be degraded or detoxified rapidly.

Changes in toxicity of the waste/soil mixture to soil microbial activity can be monitored using the short term bioassay procedures described in Table 5.1 for the determination of acute toxicity and initial loading rates. The assays are performed through incubation time and the results are compared to those obtained from a control soil. For organic wastes, stimulation of activity in assays, for example respiration and dehydrogenase which rely on heterotrophic metabolism, may be observed as microbial communities develop the capacity to degrade part or all of the waste. Assays should be continued for two or more weeks after activity has apparently returned to control levels in assays where stimulation was observed to assure that toxicity is not expressed after the stimulatory substrate has been exhausted. An increase followed by a decrease in toxicity of the soil/waste mixture may be observed. Initially, assays may need to be performed weekly. The frequency of analysis using assays may be based on the rate of change of toxicity with soil incubation time. Decreasing toxicity of the soil/waste mixture may be observed over a period of time until the toxicity is at a level that is statistically indistinguishable from that in the control soil.

Toxicity in the water soluble fraction (WSF) of a soil/waste mixture or in the leachate is especially important from a public health standpoint. Water leaching from the treatment zone should be free of toxicity, including genotoxicity. The Microtox™ assay appears suitable for determining water soluble toxicity in the waste, the waste/soil mixture, and the transformation or degradation products of the treatment process. Other assays, including higher organism assays, may also be considered (Table 5.1). Tests with higher plants and animals have the potential of showing the integration of physiological effects of toxicants on the whole organism, although these tests are more expensive and more difficult to perform than the microbial assays described above.

Mutagenicity of the WSF should also be evaluated periodically throughout the study. The accumulation of water soluble mutagens in laboratory treatability studies may limit loading rates. Mutagenicity of the WSF should be evaluated before each waste reapplication event. In field studies, mutagenicity of the soil-pore liquid at the bottom of the treatment zone may be evaluated periodically. The Ames Salmonella typhimurium mammalian microsome (Maron and Ames 1983), the Bacillus subtilis (Kada et al. 1978) and/or the Aspergillus nidulans (Scott et al. 1982, Kafer et al. 1982) mutagenicity assays are recommended for mutagenicity testing of soil-pore liquid based on the previous use of these assays in hazardous waste land treatment research. Other assays may be used if their applicability can be demonstrated. The separatory funnel liquid-liquid (method 3510) extraction procedure of the U.S. EPA (1982) is recommended for use in mutagenicity assays.

Loading rates used in the field verification study should be adjusted based on the detoxification rates observed in the laboratory studies.

5.6 IMMOBILIZATION OF WASTE CONSTITUENTS IN THE SOIL TREATMENT MEDIUM

The affinity of a chemical substance for solid surfaces is an important factor affecting its environmental movement and ultimate fate. Chemicals that adsorb tightly to soil are less subject to environmental transport in the gaseous (volatile) or solution (leachate) phases.

A number of laboratory tests consider the effects of soil adsorption on mobility. Tests most frequently used include adsorption isotherms, soil thin layer chromatography (TLC), and soil columns. Two tests recommended for use in the Federal Register (Volume 44, No. 53, March 16, 1979) are the isotherm and TLC Methods. These tests were selected for their relatively low cost, uncomplicated test procedures, wide usage and acceptance, and low labor requirements. Procedures for conducting isotherm and TLC analyses, data manipulation, and calculations are given in the reference to the Federal Register cited above. Both tests are also recommended for use by the Pesticide Guidelines (U.S. EPA, 1978) for obtaining information concerning the mobility of chemicals in soil systems. The use of isotherm and TLC procedures also supports the standards identified in Part 264.272(3)(iv).

Although soil columns have also been used to assess the mobility of chemicals in the environment, the following cautions were identified in the Federal Register (Volume 44, No. 53, March 15, 1979): (a) the difficulty of standardizing column packing, (b) the large amounts of soil and chemical required, and (c) the excessive time and labor requirements. If soil column studies are used as part of an LTD, these cautions should be recognized and addressed at the beginning of the study. The uniformity of column packing among a set of experimental columns may be evaluated using tracer studies to determine hydraulic detention time and extent of dispersion or deviation from plug-flow conditions. Procedures for evaluating flow characteristics for column reactors are included in standard environmental engineering and chemical engineering textbooks.

When column studies are used for evaluating treatment, it is recommended that a mass balance for each column be conducted that includes mobility and decay of hazardous constituents within the soil matrix. Constituent concentration through depth of each column and the time interval required to reach the measured depth should be recorded. Results may be expressed in terms of the relative transport of hazardous constituents for all columns in order to select design/management options that maximize treatment (minimize transport), and for determination of PHCs for each design/management combination. Using this procedure and procedures for determining toxicity of the waste to the treatment soil allows calculation of the soil/site assimilative capacity (SSAC) for each design management option evaluated.

A specific type of column study for land treatment evaluation is the barrel lysimeter (U.S. EPA 1984). A barrel lysimeter is a large, undisturbed soil monolith enclosed by a water tight, waste compatible casing, and equipped with leachate collection devices.

Because of the requirement for partitioning data in the mathematical model proposed for conducting LTDs, the procedures for conducting soil isotherms for determining partitioning coefficients using laboratory analyses are discussed here, and are based on the procedures discussed in the Federal Register (Volume 44, No. 53, March 16, 1979). Although not described here, TLC and soil column testing may also be used for the determination of partitioning data for land treatment demonstrations. The specific procedures and approaches for obtaining mobility information using TLC, soil columns, estimation methods, etc., should be chosen in coordination with the permit writer in order to determine how the information can best be used in support of the land treatment demonstration.

Partitioning information, which is expressed in terms of relative concentrations of constituents in oil, air, and soil phases relative to the aqueous phase, is used to evaluate the:

1. effect of the three phases (soil, air, and oil) on the concentration of hazardous constituent(s) in the leachate;

2. effect of waste and soil type on immobilization;

3. effect of soil horizons (depth) on immobilization, and;

4. effect of design and operation parameters on immobilization.

The partition coefficients required for the model include: Ko = partitioning of constituents between oil and aqueous (waste) phases; Kd = partitioning of constituents between soil and aqueous phases; and Kh = partitioning of constituents between air and aqueous phases.

It is recommended that these partition coefficients be obtained in laboratory analyses using the actual site soil and candidate waste(s). This approach supports the standards stated in Part 264.272(c)(1)(i and iv). Individual constituents that have been identified in the candidate waste(s) may also be used as pure compounds in these analyses to obtain the necessary information. The use of the site soil, however, is required in order to support Part 264.272(c)(iv).

Separate plots of the concentration of constituent(s) in each phase versus the concentration of constituent(s) in the aqueous phase at equilibrium conditions and at constant temperature provides a means for calculating each partition coefficient required. The partition coefficients are calculated as the slope of the line for each plot, as follows:

$$Ko = \frac{\text{constituent(s) concentration in oil phase}}{\text{constituent(s) concentration in aqueous phase}}$$

$$Kd = \frac{\text{constituent(s) concentration in soil phase}}{\text{constituent(s) concentration in aqueous phase}}$$

$$Kh = \frac{\text{constituent(s) concentration in air phase}}{\text{constituent(s) concentration in aqueous phase}}$$

The partitioning between oil (waste) and aqueous phases is evaluated using a procedure developed by McKown et al. (1981) for assessing the potential for mobility (leaching) of purgeable and semi-volatile organic priority pollutants from waste materials. The general approach is similar to that of the U.S. EPA Extraction Procedure (EP) and the proposed American Society for Testing and Materials (ASTM) leaching tests. Samples of waste and the leaching medium (distilled water) are mixed. The aqueous layer is then separated and analyzed. The partitioning between the oil (waste) phase and the aqueous phase can be determined by comparing the concentration of constituents in the waste with the concentration of the same constitutents in the aqueous phase.

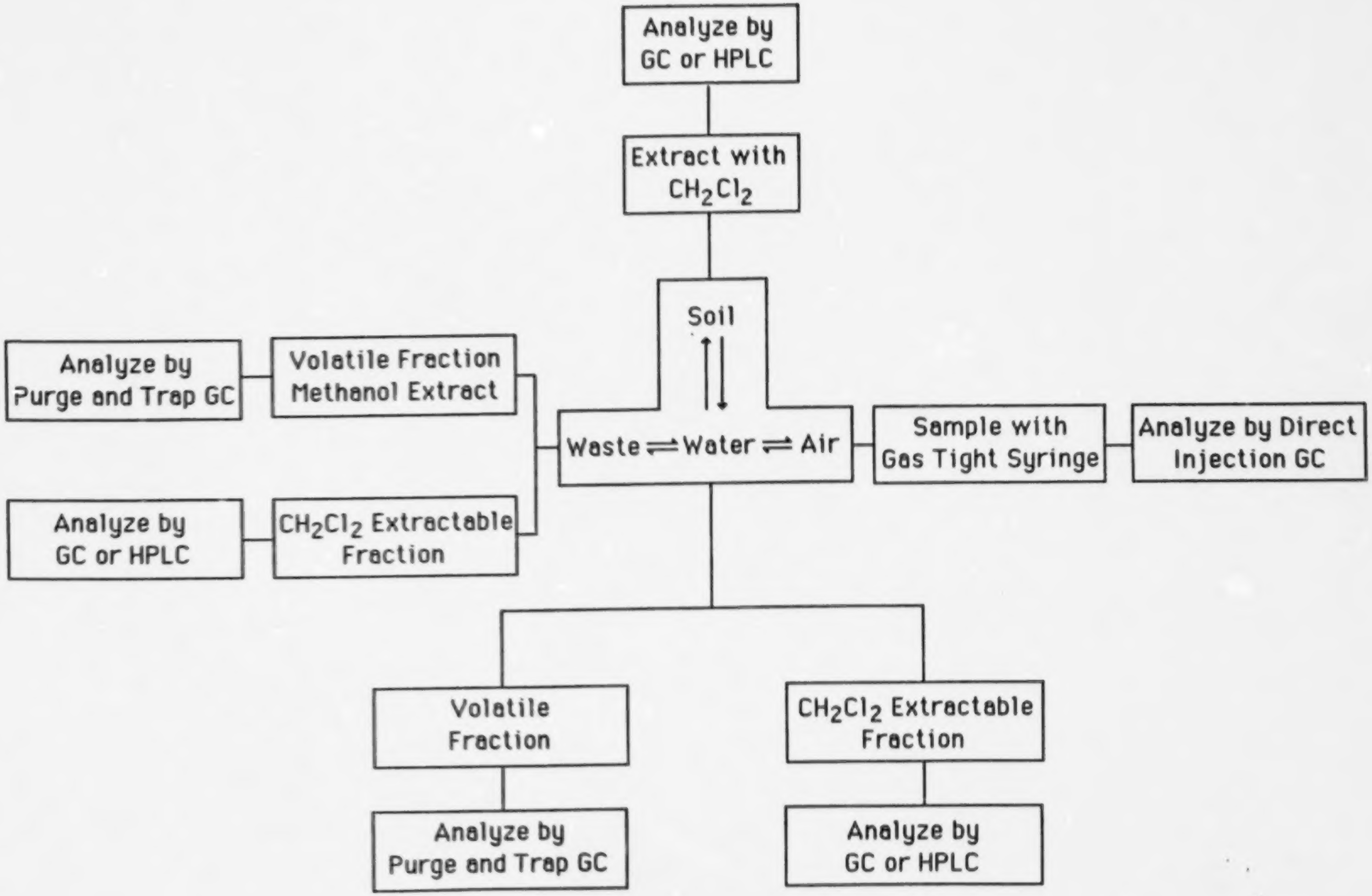
The partitioning between soil and aqueous phases is obtained by conducting a soil isotherm analysis using the treatment demonstration site soil and the aqueous phase obtained in the oil (waste):aqueous partitioning analysis. A typical method of conducting an isotherm determination is described in Weber (1971). The Pesticides Guidelines (U.S. EPA 1978) also list references to procedures for adsorption evaluations. The protocol described in this LTD Guidance Manual is based on the method described in the Federal Register (Volume 44, No. 53, March 16, 1979), and on the Environmental Engineering Unit Operations and Unit Processes Laboratory Manual (1975).

The partitioning between water and air phases may be evaluated by conducting an equilibrium partitioning analysis using the aqueous phase generated in the determination of Ko. Use of this aqueous phase permits the evaluation of air:water partitioning coefficients, Kh, as they may be affected by interactions of waste-specific contaminants existing in the extract. Such partitioning experiments should be conducted via headspace analysis equipment or simpler controlled volume, sealed sample vials maintained at constant temperature for a time period during which liquid/gas phase equilibrium is reached. Following equilibrium, both phases are analyzed for specific constituents of interest and partition coefficients are determined based on the ratio of constituent concentrations in the liquid and gas phases. A flow chart of a typical analyses scheme for partition coefficient determinations is shown in Figure 5.1.

Alternatively, partition coefficients obtained from standard references for simple water:chemical mixtures may be used for Ko, Kd, and Kh values. However, this approach does not take into account the potential interactions of waste specific contaminants occurring in the complex hazardous waste matrix.

5.6.1 Experimental Aparatus for Determination of Partitioning Between Oil Phase and Aqueous Phase (Ko)

Each experimental unit consists of a glass reactor containing waste as it will be applied to the site soil. Liners for screw cap reactors should be Teflon™. Distilled water is used for the leaching medium for simulating natural conditions. The unit is sealed and placed on a rotary mixer (tumbler) of the National Bureau of Standards (NBS) design type. Samples are tumbled at approximately 30 rpm for 22 hours + 2 hours. Extracted samples are allowed to settle for 30 minutes and the supernatant is



Analyze by GC or HPLC
Extract with CH_2Cl_2
Soil
Waste ⇌ Water ⇌ Air
Sample with Gas Tight Syringe
Analyze by Direct Injection GC
Volatile Fraction Methanol Extract
Analyze by Purge and Trap GC
CH_2Cl_2 Extractable Fraction
Analyze by GC or HPLC
Volatile Fraction
Analyze by Purge and Trap GC
CH_2Cl_2 Extractable Fraction
Analyze by GC or HPLC

Figure 5.1. Sample preparation and analysis scheme for the determination of Kh, Kd, and Ko.

centrifuged prior to analysis. Test units are set up in duplicate for each candidate waste.

5.6.2 Experimental Procedure for Determination of Ko

1. Prepare glass reactors by adding waste (wet weight) and distilled water (volume) to each duplicate reactor making sure that no head space results upon sealing. An example schedule is presented below. The amount of waste used can be varied, however, the suggested ratio of waste to water should be appropriate for most determinations.

Reactor Number	Waste	Water
1	1000 g	1000 ml
2	1000 g	1000 ml
3	1000 g	1000 ml
4	1000 g	1000 ml
5	1000 g	1000 ml
6	1000 g	1000 ml
7	500 g	1500 ml
8	500 g	1500 ml
9	100 g	1900 ml
10	100 g	1900 ml

2. Tumble test units at approximately 30 rpm for 22 hours + 2 hours at room temperature (22°C + 2°C).

3. Remove the test unit and allow to settle for 30 minutes.

4. Centrifuge the supernatant for each reactor at high speed (at least 20,000 g) for 10 minutes. The aqueous equilibrium solution should be stored at or below 4°C.

5. Reserve Reactors 1 through 4 for analyses to determine Kd and Kh values.

6. Analyze for concentrations of constituents of concern in the supernatant for Reactors 5 through 10 for determination of Ko.

7. Refer to data handling section (Section 5.6.7) for calculations of Ko values.

8. Use the supernatant from Reactors 1 and 2 for conducting analyses to obtain the partitioning between soil and water, i.e., Kd. This is accomplished by conducting isotherm analyses using the site soil and the complex waste aqueous extract supernatant.

9. Use the supernatant from Reactors 3 and 4 for conducting analyses to obtain the partitioning between air and water, i.e., Kh, as per Experimental Procedures for Determination of Kh presented below.

5.6.3 Experimental Apparatus for Determination of Partitioning Between Soil Phase and Aqueous Phase (Kd)

Sealable glass reactors should be used. Screw cap reactors should use Teflon™ liners. Reactors are sealed and placed on a shaker or tumbler for mixing at 22°C ± 2°C. Soils should be sieved with a 100 mesh stainless steel or brass screen before testing.

5.6.4 Experimental Procedure for Determination of Kd

1. Use four aqueous subsamples of each supernatant obtained from Reactors 1 and 2 for determination of Kd (approximately 250 ml), for a total of eight samples (four duplicates). The following schedule is suggested although other combinations may be considered:

Sample	Aqueous Phase	Soil
1	250 ml	0.5 g
2	250 ml	0.5 g
3	250 ml	1.0 g
4	250 ml	1.0 g
5	250 ml	2.0 g
6	250 ml	2.0 g
7	250 ml	10.0 g
8	250 ml	10.0 g

2. Immediately after addition of the solution, assuring that no headspace exists, the containers should be vigorously agitated with a vortex mixer or similar device. The containers should be equilibrated in the rotary tumbler for 22 ± 2 hours.

3. After equilibration, the suspensions should be centrifuged at a high speed (at least 20,000 g) for 10 minutes. The aqueous equilibrium solutions should be stored at or below 4°C.

4. The chemical adsorbed on the soil surface should be extracted with an organic solvent in which the test chemical(s) is soluble, and a mass balance should be performed. A volume of organic solvent equal to the original volume of aqueous solution (used to attain equilibrium) should be added to the adsorbent so that no headspace exists, and the containers shaken vigorously for 10 minutes. The mixture should then be centrifuged at a minimum of 20,000 g for 10 minutes. This extraction procedure should be performed three times.

5. The aqueous phase and the organic solvent extracts should be analyzed for the constituents of concern. If the mass of constituents in the aqueous and/or the solvent phases are too low, concentration of each phase must be carried out using standard techniques, i.e., K.D., purge and trap, etc.

5.6.5 Partitioning Between Aqueous Phase and Air Phase (Kh)

Glass reactors with sealable Teflon™ septum caps should be used. A known amount of aqueous extract solution is added to provide a variable air phase volume in the reactors. The reactors are maintained at constant temperature of 22°C ± 2°C for 22 ± 2 hours to ensure equilibrium is reached.

5.6.6 Experimental Procedure for Determination of Kh

1. Use four aqueous subsamples of each supernatant obtained from Reactors 3 and 4 for determination of Kh, for a total of eight samples. Four volumes of supernatant should be used to provide a variable gas volume over the liquid that allows the determination of true equilibrium within the samples. The following schedule is suggested although other combinations may be considered:

Sample	Aqueous Phase	Gas Phase
1	50 ml	75 ml
2	50 ml	75 ml
3	62.5 ml	62.5 ml
4	62.5 ml	62.5 ml
5	75 ml	50 ml
6	75 ml	50 ml
7	85 ml	40 ml
8	85 ml	40 ml

2. Immediately after addition of the solution to the unit, the upper Teflon™-lined cap should be sealed and the unit should be placed in a constant temperature environment for a 22 ± 2 hour incubation time.

3. Upon completion of incubation, the gas phase is sampled (1-4 ml) with a gas-tight syringe and analyzed by direct injection gas chromatography. Duplicate samples should be taken for GC analysis, and efforts should be made to minimize volume taken for each sample to prevent a significant vacuum from occurring within the sample vial.

4. The aqueous phase should be analyzed immediately for contaminants of concern following solvent extraction and/or concentration (purge and trap, KD concentration, etc.) if the concentrations of contaminants in that phase are too low for accurate quantification following equilibrium partitioning.

5. A mass balance can then be performed using data from the aqueous and air phases to indicate the accuracy of the method.

6. If the concentrations of constituents in either of the two phases are too low after equilibrium to obtain accurate results larger air/liquid partitioning vessels (500 to 1000 ml) could be used to provide large phase volumes for the concentration step prior to quantification.

5.6.7 Three Phase Partitioning Method for Ko and Kh Determination

An alternative to separate phase partitioning experiments using waste, aqueous, and air phases is possible if equilibrium concentrations of contaminants of interest are readily quantifiable without significant phase concentration. This method utilizes glass crimp top vials with Teflon™-lined septa, as described above, for the equilibration of the waste, aqueous, and air phases as shown in Figure 5.2.

5.6.8 Experimental Procedure for the Combined Contamination of Ko and Kh

1. Prepare glass serum bottles by adding the approximate waste (wet weight) and distilled water (volume) to each duplicate reactor according to the following suggested schedule for each candidate waste:

Sample	Aqueous	Waste
1	75 ml	0.5
2	75 ml	0.5
3	75 ml	1
4	75 ml	1
5	75 ml	5
6	75 ml	5
7	75 ml	10
8	75 ml	10

2. Immediately after addition of the waste and distilled water to the bottles, the Teflon™-lined cap should be sealed and the bottles should be tumbled for 22 ± 2 hours in a rotary mixer at approximately 30 rpm.

3. After tumbling, the bottles are centrifuged at 2000 rpm for 30 minutes.

4. Upon completion of centrifugation the gas phase is sampled (1-4 ml) using a gas tight syringe. Duplicate samples should be taken for GC analysis, and efforts should be made to minimize volume taken for each sample to prevent a sigificant vacuum from forming within the serum bottle.

5. Aliquots of the aqueous phase are taken immediately after headspace sampling. Duplicate analyses for volatile constituents should be conducted using purge and trap procedures, while solvent extraction/concentration procedures should be conducted for nonvolatile constituents of interest using the balance of the aqueous phase.

6. Finally, aliquots of the waste phase should be taken, following aqueous phase sampling, for use in volatile and/or nonvolatile constituent quantification in the equilibrated waste phase.

7. A Kd can be evaluated from the equilibrated aqueous phase generated from this procedure if a larger initial aqueous phase volume (400 ml) is utilized. This aqueous phase is used to determine Kd according to the procedures described in Section 5.6.4.

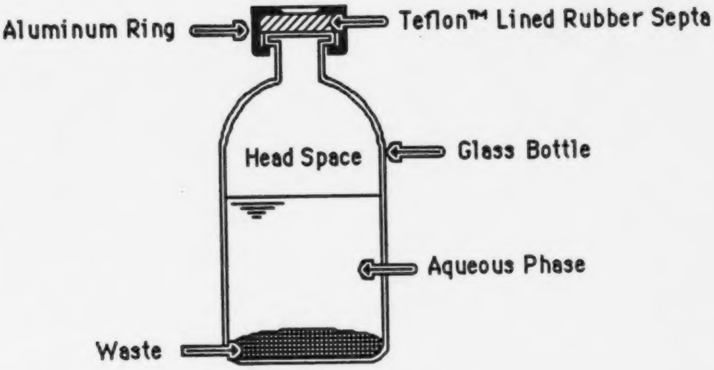

Aluminum Ring
Teflon™ Lined Rubber Septa
Head Space
Glass Bottle
Aqueous Phase
Waste

Figure 5.2. Apparatus for three-phase partitioning coefficient determinations.

5.6.9 Data Handling

For each partition coefficient, Ko, Kd, and Kh, the determination of the value of the coefficient is determined from a plot of the concentration of a constituent in the aqueous phase (x-axis) versus the concentration of the constituent in the relevant phase (y-axis). Three plots will be generated, one plot for determination of each partition coefficient. Each partition coefficient is calculated as the slope of the line. Values for the partition coefficients for each hazardous constituent serve as input to the LTD mathematical model presented and discussed in Chapter 4 of this manual.

5.7 DEGRADATION OF WASTE CONSTITUENTS IN THE SOIL TREATMENT MEDIUM

Loss rates are generally based on first order kinetic constants derived from laboratory or field studies. Methods and procedures for laboratory studies that can provide data for the calculation of rate constants are presented below.

A plot of the disappearance of a constituent, originally present in the waste and in the waste/soil mixture immediately after waste application, versus treatment time provides the following information:

(1) The reaction order of the degradation process (generally either zero order or first order);

(2) The reaction rate constant, μ (mass constituent/mass soil-time for zero order reactions or 1/time for first order reactions);

(3) The half-life ($t_{1/2}$, time) of each constituent of concern.

Degradation information should be collected at constant temperature, and through at least one complete cycle of application and treatment prior to reapplication. Biodegradation rates for each constituent of concern must be calculated, as well as the biodegradation rate for the oil phase of the waste. Degradation rates are converted into half-lives for constituents and for the oil phase.

Degradation information, which is normally reported as half-life in the soil, is used to evaluate:

(1) Effect of degradation on the attenuation of constituent transport through the treatment zone; and

(2) Effect of design and operation parameters on constituent degradation and attenuation of resultant constituent transport through the treatment zone (including loading rate, loading frequency, control of soil moisture, amendments to maximize degradation, etc.).

5.7.1 Hazardous Constituent Reduction Evaluation Techniques

5.7.1.1 General Experimental Approach--

Hazardous constituent reduction experiments using methods accounting for contaminant vapor loss from the soil are recommended if significant amounts of volatile constituents exist in the waste to be evaluated for land treatment. A complete experimental set-up might include, for example, degradation units consisting of 600 ml glass beakers containing 200 g of prepared soil (air-dry weight), along with air emission flask units consisting of 500 ml ground glass stoppered Erlenmeyer flasks in which up to 200 g of prepared soil is added. The units are arranged in sample sets for sacrifice at selected intervals during the duration of the experiment (126 days). Waste-soil in the sacrificed units is extracted and analyzed for TOC and specific organic constituents to evaluate PHC reduction with time.

Test units are routinely set-up in triplicate for each of three levels of waste loading plus a blank for each sampling interval (triplicates for the air emission samples for each waste loading only). The units are typically incubated at room temperature (22°C + 2°C) in the dark. Four sample sets of the degradation units are prepared for sacrifice, extraction and analysis, and data calculation at selected test intervals, while only a portion of the air emission units are sacrificed at 42 days with the balanced dismantled and evaluated at the end of the study.

5.7.1.2 Evaluation of Biodegradation--

5.7.1.2.1 Experimental Apparatus--Each experimental degradation unit consists of a 600 ml glass beaker containing 200 g of prepared soil (air-dry weight). Following an initial acclimation period, each unit is charged with one of the selected loadings of waste. The units are arranged in sample sets for sacrifice at selected intervals during the duration of the experiment (126 days). Waste-soil in the sacrificed units are analyzed for TOC and specific organic constituents to evaluate apparent degradation potential.

The experimental apparatus for air emission measurements is shown in Figure 5.3. The system consists of the 500 to 1000 ml Erlenmeyer flask with a fitted glass aeration cap through which high quality breathing air enters the flask through Teflon™ tubing. The purge air flows over the surface of the soil-waste mixture contained within the flask and exits the aeration cap through an effluent tube close to the top of the flask. The flow path and configuration of the flask ensures effective mixing over the surface of the soil. Effluent purge gas containing volatile constituents from the soil-waste mixture leaves the flask through Teflon™ tubing, passes a glass T used for split stream sampling, and is then conducted via tygon tubing to a vent for discharge away from the experimental area. Split stream sampling is conducted through the glass T's in the flask effluent line by using a constant volume sample pump in conjunction with sorbent tubes, sample bulbs, etc., connected to the pump via a balanced capillary flow controlled glass and Teflon™ sampling manifold.

5.7.1.2.2 Experimental Procedure for Apparent Degradation Measurements--

a. Prepare experimental units for each design/management combination.

b. Adjust the soil moisture content in each unit to 70 percent (except where soil moisture is evaluated as a management option); record unit weight.

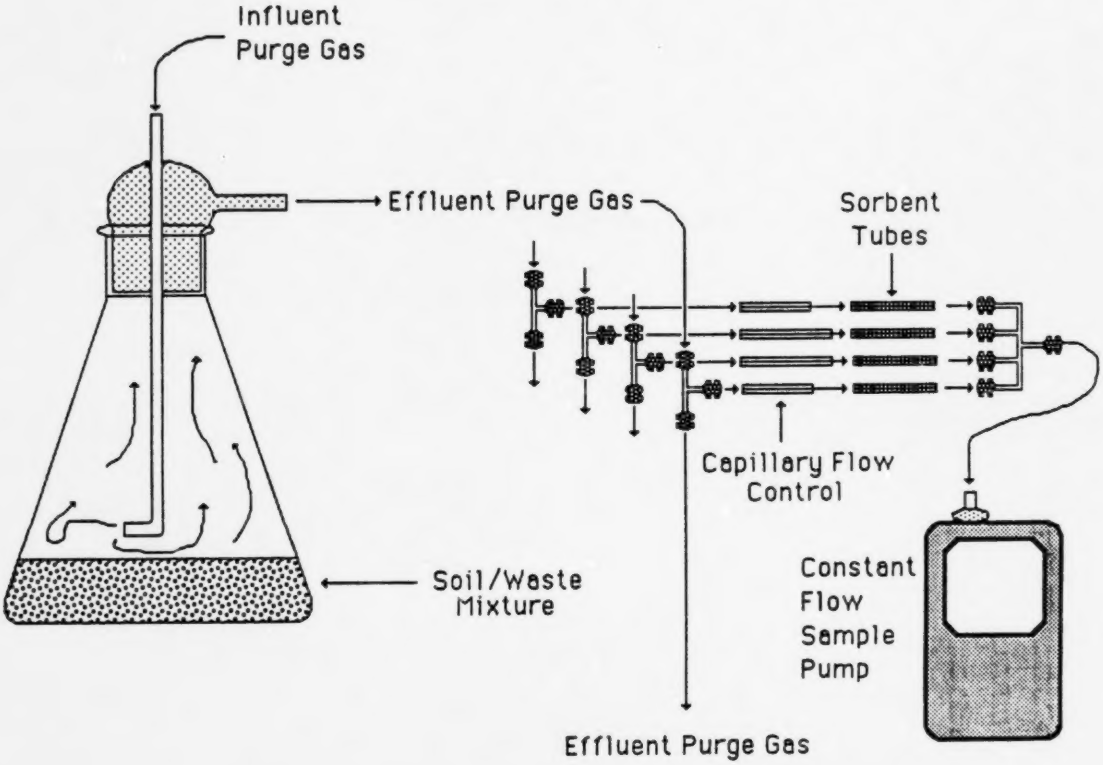

Influent Purge Gas
Effluent Purge Gas
Sorbent Tubes
Capillary Flow Control
Soil/Waste Mixture
Constant Flow Sample Pump
Effluent Purge Gas

Figure 5.3. Laboratory flask apparatus used for mass balance measurements.

c. Place test units in dark at room temperature and allow to acclimate for 10 days while maintaining favorable moisture content.

d. Following acclimation, charge each test unit with its selected loading (wt. %) of waste and mix thoroughly (36 units will receive 1 of 3 selected waste charges and 12 will receive no waste charge).

e. Arrange the test units in 6 sample sets consisting of 2 units for each charge and 2 control soil blanks (8 test units).

f. Place 5 sample sets in the dark at room temperature to begin the test; sacrifice the Day 0 sample set for organics extraction and TOC analysis.

g. Check the moisture content of each unit weekly and adjust to 70 percent water-holding capacity by adding deionized water.

h. Aerate each unit by mixing the total contents thoroughly every 14 days.

i. Sacrifice sample sets so that a minimum of 6 points are used to generate the degradation plot. Sampling on days 7, 21, 42, 84, and 126 may allow completion of the experiment. If results indicate sufficient data have been generated, the PHC experiment can be terminated following data calculations for any sample set.

5.7.1.2.3 Experimental Procedure for Volatilization Corrected Degradation Rates--

a. An experimental run is initiated by first placing an amount of the actual field soil within 12 flask units, the magnitude and procedure of which is dependent upon the application method, i.e., surface or subsurface, being simulated during the run. If subsurface application is to be simulated, approximately 200 g of soil is placed in the flask, waste is added following the 10 day acclimation period as described for the degradation studies above, acclimated soil of 70 percent moisture content is then immediately placed above the waste application point to a depth simulating the actual subsurface injection depth to be used in the field, and the flask units are quickly capped. If surface application is simulated, waste is added to the 200 g of soil in the flask, is quickly mixed, and the flask units are quickly capped.

b. Once capped, the purge gas should be initiated at a controlled rate of 200 ml/min, and initial emission measurements are begun by drawing a constant volume sample of flask effluent gas through the sampling/collection system via a constant volume sample pump and a balanced, capillary flow controlled, four-place sampling manifold (three samples plus a blank). This procedure allows the concurrent sampling of all flask units for the same period of time and during the same time period over the volatilization run.

c. Sample pump rate and purge gas flow rate are measured before each sampling event via a bubble tube flow meter and the duration of the sorbent tube sampling is recorded for accurate soil loss rate calculations.

d. Upon completion of the sampling event, sampling tubes, bulbs, etc., should be stored as recommended by EPA prior to analysis via standard procedures appropriate for the specific sampling/concentration method used.

e. The sampling and analysis procedure is repeated at selected time intervals following waste addition corresponding to the anticipated log decay in soil loss rates. A recommended sampling schedule is as follows:

0, 15 min, 1 hour, 2.5 hours, 10 hours, 1 day, 10 days, 21 days, 80 days, and 126 days

If results indicate undetectable air release rates after 10 days of sampling, this portion of the study may be terminated. If blank soils show insignificant levels within the first day of sampling, their use may also be discontinued. Appropriate blanks and spikes must be used throughout the sampling period, however, to maintain QA/QC procedures for the method.

f. The moisture content of these units should be checked weekly and adjusted to 70 percent water holding capacity by adding deionized water.

g. One flask from each loading rate should be sacrificed following the 21 day sampling event to allow correlation with degradation studies regarding residual soil mass levels of contaminants in the applied waste.

5.7.1.3 Data Calculations--

For each of the selected operating/management and waste loading conditions evaluated, the degradation kinetic parameters, and half-life ($t_{1/2}$ in days) for first order kinetics or the rate of transformation (r in mg/kg/day) for zero order kinetics, are calculated from specific constituent and gross parameter data after being corrected for volatilization losses measured during the study. Mean concentrations for the duplicate units are used in all calculations.

For each PHC, a plot of cumulative mass collected in the emission flask effluent gas versus time is made. These cumulative mass values are calculated from the measured soil release data (mass/area/time), the soil surface area exposed to the purge air, the fraction of purge air actually sampled, and the cumulative time during effluent sampling. The cumulative mass values are then used to correct degradation data for volatile emission losses by subtracting them from the total PHC mass change as indicated from beaker degradation studies.

For each PHC, a plot of mean volatilization-corrected concentration versus time is made. If a straight line plot results, then zero-order kinetics are indicated and the rate of degradation is computed from the slope of the straight line.

$$f = C_1 - C_2/t_2 - t_1 \qquad (5.1)$$

where:

C_i = the volatilization-corrected concentration coordinate of point i on the straight line in mg/kg

t_i = the time coordinate of point i on the straight line, days

If zero order kinetics do not fit the data, plot the ratio of the mean volatilization-corrected concentration at day t to the mean concentration at day 0 versus time on semi-log paper (time is plotted on the linear scale). If a straight line results from a plot of this type, first-order kinetics are indicated, and the slope of the relationship of the natural logarithm of contaminant concentration at time, t, divided by contaminant concentration at time zero versus time represents the first order degradation rate for that constituent with units of 1/time.

The half-life coefficient, $t_{1/2}$ (time), represents the length of time required for a constituent, C, to decay to one-half of its original concentration, C_o:

$$C = C_o \, 2^{(-t_{1/2})} \quad (5.2)$$

where:

C_o = the initial concentration of a constituent in soil (mg/kg)

C = the volatilization-corrected concentration of constituent in soil at time t (mg/kg)

$t_{1/2}$ = half-life of the constituent in soil (time)

Because the above relationship is not a linear function, there is no convenient relationship between the half-life and the zero order rate coefficients; however, the half-life may be calculated from the first order rate coefficient by the following formula:

$$t_{1/2} = \ln (0.5)/(-\mu_1) = 0.693/\mu_1 \quad (5.3)$$

where:

$t_{1/2}$ = half-life of waste constituent in soil (time)

μ_1 = first order volatilization-corrected degradation rate, slope of plot of logarithm of concentration versus treatment time (semi-logarithm plot) with units of 1/time

For those cases in which neither zero order nor first order kinetics apply, the plot of volatilization-corrected concentration versus time is simply reported.

Effects of design and operation parameters on contaminant degradation is evaluated from degradation rate and $t_{1/2}$ data from degradation experiments conducted under various design and operation conditions. For example, evaluation of the effect of moisture content on corrected waste degradation at a design application rate can be determined by conducting laboratory scale degradation studies at three soil moisture contents. Optimal moisture conditions for such an experiment can be determined from analysis of reaction rate constants and/or $t_{1/2}$ values measured at each condition investigated. The moisture content producing a maximum corrected degradation rate and minimal $t_{1/2}$ for the PHCs in the waste would then be selected for use in field verification studies.

Similar laboratory experiments can also be conducted for determining conditions for nutrient addition, organic amendment, soil pH control, etc., that result in maximizing of land treatment activities.

5.7.1.4 Evaluation Using Laboratory Scale Microcosm Systems--

5.7.1.4.1 Introduction--Laboratory data may be collected using column or microcosm systems if it is desired that laboratory equilibrium partitioning data and model prediction information be evaluated on a laboratory scale prior to actual field plot studies. It should be recognized, however, that while column studies do provide a means of investigating land treatment system dynamics, results should be expected to be highly variable due to variability in packing methods, soil uniformity, etc., as discussed above. Results often preclude rigorous quantification of transport and degradation phenomenon, but do allow semi-quantitative evaluation of the scale of various interaction pathways expected to affect waste constituents applied to the actual land treatment site. The cost and complexity of column or microcosm systems should be weighed against the value of data collected in such a laboratory system that may be collectable at an experimental field site.

5.7.1.4.2 Experimental Apparatus--Air emission monitoring and quantification as a function of operating and management procedures is conducted in a controlled laboratory setting using modular, 7.62 cm I.D., beaded glass process pipe microcosm systems, with solid sorbent tubes, sampling bulbs, etc., for sample collection and/or concentration. Figure 5.4 shows a typical microcosm unit consisting of two 15.25 cm long body sections, along with removable bottom and top cap sections for ease of unit assembly and disassembly for cleaning. Sections of each unit are connected via Teflon™-lined pipe clamps to provide an air and water tight seal at all joints. The top cap section has four glass inlet tubes to provide inlet and outlet ports for purge gas flow, a port for connection to a Magnehelic or manometer for cap pressure determinations, and a port for head space temperature and gas composition determinations. Brass Swedgelock™ fittings with Teflon™ ferrules are used at all connections, with Teflon™ tubing used for all transfer lines to the point of split stream sampling. Tygon™ tubing is used downstream of the split stream point for purge gas venting, with venting conducted to an enclosed hood for discharge from the experimental area.

High quality breathing air is utilized as purge gas to eliminate the possibility of oxygen limitations that may occur to microbial process carried out during the volatilization runs. A series of four microcosms are connected to a single purge gas source via balanced glass Ys, with flow balance checked via Magnehelic or manometer readings to ensure equal flow to each microcosm unit. Microcosm units are placed in a constant temperature water bath or within a constant temperature room to eliminate temperature variation during a given run.

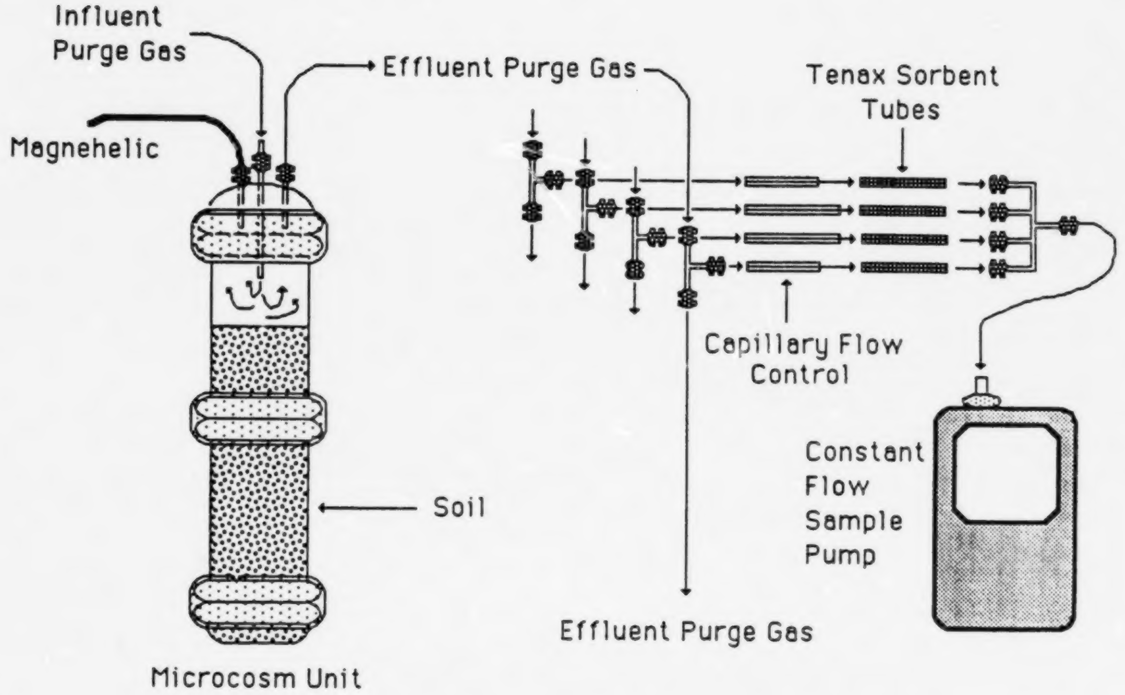

Influent Purge Gas
Effluent Purge Gas
Tenax Sorbent Tubes
Magnehelic
Capillary Flow Control
Constant Flow Sample Pump
Soil
Effluent Purge Gas
Microcosm Unit

Figure 5.4. Laboratory microcosm apparatus used in laboratory AERR model validation studies.

5.7.1.4.3 Experimental Procedure for Microcosm Studies--

a. An experimental run is initiated by first placing a given depth of soil within a microcosm unit, dependent upon the application method, i.e., surface or subsurface, being simulated during the run. A maximum application of depth of approximately 15.24 cm is possible with the two piece body shown in Figure 5.4 with deeper application depths possible with additional body units connected in series.

b. Soil depth and mass readings are taken for bulk density determinations.

c. Waste is then applied to the units in as uniform a fashion as possible. The application rates used are based on a weight percent of waste with respect to the top 6 inches of the soil material the waste is applied to. If subsurface injection is to be simulated, the appropriate amount of soil is added to the unit to provide the desired soil depth above the application point.

d. The units are then capped, sealed air tight, and purge gas is initiated and maintained constant at 300 ml/min/microcosm during the volatilization experiments.

e. Microcosm gas sampling is conducted at selected time intervals following waste application as described above for volatilization-corrected degradation rate flask studies (5.7.1.2.3 b through d).

f. Data related to the physical conditions of the microcosm systems are collected at each sampling time and include air and water bath temperature, height of the capillary rise observed above the injection point, and depth of the waste wetting front below the soil surface.

g. When used in conjunction with degradation and leaching rate measurements, columns must be sacrificed at selected intervals, as described above, to allow soil extraction for mass balance determinations.

CHAPTER 6

MONITORING TREATMENT PERFORMANCE IN THE FIELD

6.1 PURPOSE OF FIELD VERIFICATION STUDY FOR NEW AND ISS FACILITIES

The purpose of a field plot study is to verify the effectiveness of waste treatment under field conditions for selected design and management option(s). Field verification studies are appropriate for sites using Scenario 2 or 3 (Chapter 1) for obtaining a Part B permit. The design and management option(s) may have been selected based on the result of laboratory studies (Chapter 5) and/or model results (Chapter 4). Alternatively, for ISS facilities, previous field scale practices that have not been evaluated with respect to the specific criteria given in Part 264 may be selected. However, for ISS facilities, if the applicant selects a design/management combination that is different from previous practice(s), with respect to changes in unit processes, application rates, or use of soils, the use of laboratory studies and/or model estimation is strongly encouraged for evaluation of potential treatment effectiveness before conducting a field verification study. The field evaluation is based on monitoring soil cores and soil-pore liquid to detect losses. The use of the PHCs identified through laboratory or other studies may also be verified in the field studies.

The field plot study has the following components:

Design parameters	- application rate(s) - application frequency - application method(s)
Management options	- controlling soil pH - enhancing microbial activity - enhancing chemical reactions - controlling soil moisture
Site selection	- site location - number of sites needed
Monitoring	- soil core - soil pore liquid - waste analysis - groundwater (optional)
Data interpretation	

The field verification study is intended to provide the following specific information:

a) The effectiveness of design parameters and management options for the degradation, transformation, and immobilization of hazardous constituents by monitoring soil cores and soil-pore liquid.

b) Whether significant concentrations of hazardous constituents occur below the treatment zone and in groundwater.

c) If current ISS site loading rates and frequencies are compatible with local site conditions.

d) If current ISS management practices are suitable for local site conditions.

e) A data base for evaluating transferability of information concerning effectiveness of waste treatment from one site to another using the mathematical model proposed, or a similar model, to integrate site, soil, and waste information.

6.2 FIELD VERIFICATION STUDY ALTERNATIVES

Field verification studies may be conducted using one of the methods identified in Table 6.1. The table contains a comparison of field verification alternatives for factors including representativeness, effectiveness, and implementation aspects. Other methods may be used for field verification studies, and would need the approval of the permit writer.

As indicated in Table 6.1, field verification studies are categorized by the size of the field plot. Box plots and barrel lysimeters are small scale reactors containing experimental units that are physically separated from the surrounding site/soil. Typically a 5' x 5' wooden box plot is used. A barrel lysimeter is a cylindrical reactor containing an undisturbed soil monolith. Information concerning the collection and installation of barrel lysimeters is presented in Brown et al. (1985).

A larger field scale plot may also be used. Generally, a field scale plot may be used on an existing ISS site or new site with runon/runoff and other field conditions controlled. Usually approximately 12 ft x 48 ft in size, field scale plots allow routine full scale management practices to be applied.

It is also possible to collect and evaluate data from a full-field treatment area for ISS sites. However, as indicated in Table 6.1, the effectiveness in accurately evaluating treatment processes is generally low. This is due to the difficulty in accounting for and controlling sources of variation in sampling and treatment in full field evaluations.

Table 6.1. Comparison of Field Verification Alternatives.

Factor	Barrel Lysimeter or Box Plot	Field Scale Plot	Full Field
	Comparison Scale		
Representativeness			
Simulation of climate, soils, and operations	Moderate	Moderate	High
Effectiveness in Evaluating Treatment Processes			
Degradation	Moderate	Moderate	Low
Transformation	Moderate	Moderate	Low
Immobilization	Moderate	Moderate	Moderate
Toxicity	High	High	Low
Integrated Effects	Moderate	Moderate-High	Low
Implementation Aspects			
Variability control	High	Moderate	Low
Reproducibility	Moderate	Moderate	Low
Cost	Moderate	Moderate	High
Design/management problems	Moderate	Low	High

6.3 SELECTION OF DESIGN AND MANAGEMENT PARAMETERS

Acceptable design parameters (loading rates, loading frequencies and application methods), and operation and management options have been established at many of the land treatment facilities currently operating under interim status. These established design and management options can be used for the LTD. If a new facility is planned, methods discussed in this manual (Chapters 2 and 5) may be used to determine acceptable design parameters and operation and management options. Loading rates in field verification studies should not result in concentrations of metals in the soil greater than those recommended by the U.S. EPA (1983a), as discussed in Section 2.5.

The field test should accurately simulate the site characteristics and operating conditions, including waste, climate, topography, soils, treatment zone characteristics and likely operating practices. Results from the laboratory studies and model predictions, summarized as Cb/Tb for each constituent (Section 4.3), may be used to select one waste application design (loading rate, loading frequency and application method) and field management scheme (soil pH, soil moisture, chemical reaction, nutrients and microbial activity) that will be evaluated in the field. More than one design/management combination may also be evaluated at the discretion of the permit writer. The purpose of the field plot study is to verify the effectiveness of the selected design and management options under field conditions. Replication of each waste application and field management scheme to be tested is highly recommended. The field study should be conducted for at least one seasonal cycle for ISS units and 1-2 years for a new facility, depending on recommendations of the permit writer and results of the first year study. The study should be conducted until a 50 percent reduction in the initial concentration is experimentally observed for a majority of hazardous constituents. Special attention should be given to short-term leaching effects (generally one week to three months after waste application, with sampling closely following precipitation events).

6.4 ANALYTICAL ASPECTS OF FIELD VERIFICATION

The design plan should identify proposed statistical testing approaches for the field verification study. The analytical approach to the monitoring and analyses of field samples involves the use of Type III identification technology (GC/MS) and Type II monitoring technology (GC, HPLC). Type III analyses should be conducted at the beginning, middle, and end of the field verification study. Metals analyses should also be conducted to determine accumulation of metals in the soil profile. After initial waste application, at least 5 percent of each sampling media analyzed with type II methodology should also be analyzed with Type III technology to verify that the identification and monitoring results agree with respect to constituent identification. The PHCs selected should be monitored through time with Type II technologies.

Monitoring analyses should also include toxicity testing of the zone of incorporation (ZOI) and below treament zone (BTZ) samples using the Microtox assay or other appropriate bioassays (see Chapter 5). Bioassays of the ZOI will be used to evaluate the relative detoxification of the soil-waste mixture with time. Bioassay of BTZ samples will be used as an indicator of hazardous constituents leaving the treatment zone. If carcinogenicity is of concern with the PHCs present in a waste, the mutagenic potential of the soil-waste mixture should be monitored using a mutagenic assay such as the Ames Salmonella microsome assay (Chapter 5).

Analytical costs for the field verification study may be estimated from Table 2.6. Results of the field verification study should be evaluated and interpreted using the statistical methods discussed in Appendix B.

6.5 PLOT PREPARATION

"Uniform area" has been defined as an area of the active portion of a HWLT unit composed of soils of the same soils series to which similar wastes are applied at similar rates (Chapter 3). A rigorous soil survey will have been conducted as part of the reconnaissance study for the HWLT unit such that those soil properties that affect treatability of waste types have been identified and those areas with similar treatability characteristics have been classified as uniform. The number of field plots should be based on the number of uniform areas. Replication of field plots is recommended especially for barrel lysimeter or box plot studies. Soil monoliths for barrel lysimeters and sites for box plots should be chosen from uniform areas for field scale plots. Locations of field scale plots are also determined by choosing uniform areas based on the site soil survey. Ease of access and isolation from existing waste treatment facilities should be considered. Plots should be chosen to represent slope and drainage conditions.

The size of a box plot, barrel lysimeter, of field scale plot may vary. Box plots are generally 5 x 5 feet to allow for easy application of wastes. A barrel lysimeter is usually constructed from a 55 gallon drum. Details concerning the collection of barrel sized undisturbed soil lysimeters may be found in Brown et al. (1985). The smaller the plot, the more difficult it will be to evaluate leaching using soil-pore liquid samplers.

The size and location of field scale plots should, however, reflect full scale field operation application methods and equipment usage. The size and shape of a field scale plot may vary. For example, if a tractor with a 10 ft manure spreader is to be used for waste application, a plot that is 10 ft or 20 ft wide would accommodate the method of application. The total areas of the plot should be at least 550 ft^2. Experimental field plots should be isolated from existing waste treatment areas using berms around plots to eliminate cross-contamination and runon/runoff. Berms need to be high enough to contain or eliminate specified storm-water flow events, as required under Section 264.273(c). It is not necessary to physically separate plots intended to receive the same waste loading and frequency. Similar considerations would apply for box plots, which should be protected from runon/runoff.

Barrel lysimeters should be sheltered from normal precipitation (e.g., with an open-sided pole barn); water should be applied in specified amounts. The site water budget may be useful in terms of water added via other sources (e.g.; irrigation). After calculated losses due to runoff/evaporation have been subtracted, appropriate amounts of water may be applied according to the precipitation record.

Run-off collection can be accomplished at field scale plots in small sumps or impoundments at the low slope position of each plot. The size of the collection area is calculated based on the water balance computed for the site. Run-off collection ponds should be designed to contain run-off from the 24 hr/25 yr storm. The LTD plan should address managment of excess runoff.

The use of control plots on previously treated soil for ISS sites is recommended to allow estimation of longer term degradation, transformation, and immobilization of hazardous constituents already in the soil. A control plot is not necessary for a new site, since background conditions can be defined adequately from the test plot receiving wastes.

6.6 WASTE APPLICATION

Waste application practices used or planned for use on the full-scale land treatment unit should be used for field verification studies. Incorporation of waste should be accomplished with the same type of equipment used on the land treatment units, and corresponding tilling practices should be used.

To apply waste to a barrel lysimeter or box plot, the zone of incorporation should first be removed and carefully homogenized with the applied waste. A plastic barrier can be laid around the edge of the casing or box to prevent side channel flow. The soil-waste mixture is then replaced in 5 cm or small lifts, tamping each successive layer if necessary, to achieve field bulk density.

Normal tillage and deposition practices do not ensure a uniform distribution in field scale plots. Variability in the waste distribution in the ZOI for field scale plots may be reduced by either of two methods. A pug mill or cement mixer could be used to mix the ZOI soil and waste, followed by careful application to the soil. Care must be taken in using tilling, since large discontinuous blocks of soil containing little or no waste may be raised to the soil surface. Alternatively, applied wastes could be tilled repeatedly until a desired uniformity is achieved. Random sampling should be excluded from areas near the edge of the plot on all sides.

6.7 FIELD VERIFICATION STUDY MONITORING

A hazardous organic constituent of a waste may be volatilized, sorbed, degraded, or leached in the soil system. The goal of land treatment is to maximize sorption and degradation processes while minimizing volatilization and migration losses. Field verification plot monitoring consists of:

- soil-core sampling, for monitoring degradation, immobilization, and transformation of hazardous constituents in soils with depth;
- soil-pore liquid sampling, for monitoring losses of hazardous constituents in soil-water below the treatment zone;
- groundwater sampling, for monitoring contamination of groundwater.

Volatilization is not specifically addressed in field verification plot monitoring, because of the lack of guidance in 40 CFR Part 264.

Evaluation of results should be conducted during the performance of the LTD to allow for any necessary modifications of the monitoring schedule.

An example of a sampling schedule for a hypothetical land treatment unit is given in Appendix G.

6.7.1 Collection and Analysis for Soil Core and Soil Pore Liquid Samplers

6.7.1.1 Soil Core--

Analysis of soil cores is necessary to monitor the behavior of hazardous constituents present in the treatment zone, to identify possible degradation products, and to detect slowly migrating hazardous constituents below the treatment zone.

For barrel sized lysimeters, Dr. K. W. Brown of Texas A&M University should be contacted for details on monitoring treatment in the lysimeters.

For field scale plots, soil cores may be divided into four sections: 1) the zone of incorporation (ZOI); 2) an upper treatment zone (TR1); 3) a lower treatment zone (TR2); and 4) below treatment zone (BTZ), as described in Chapter 3. Soil survey information may indicate other subdivisions of the soil core based on soil properties relevant to waste treatment. Zone of incorporation (ZOI) soil samples and soil cores should be collected at random on each plot with the appropriate sampling device. Details concerning soil sampling are discussed in Section 3.4.2. U.S. EPA (1984) provides guidance for selection of the appropriate devices for specific soil types.

The monitoring schedule should be designed to sample soil cores at frequent enough intervals to determine whether a waste is being treated and whether hazardous constituents are passing below the treatment zone. To determine initial concentrations of hazardous constituents in the zone, a soil sample should be taken immediately after the initial waste application and incorporation and following each application thereafter. The frequency of core sampling should be based initially on mobility and degradation rates determined in the laboratory studies and predicted for field conditions using the proposed or similar model. This periodic evaluation of the soil cores between the ZOI and BTZ is made to determine the extent of mobility of hazardous constituents within the treatment zone. At specific times, the entire soil core to some point below the treatment zone (e.g., 30 cm) should be analyzed to determine if any hazardous constituents, including degradation products have migrated down the soil profile. Once a data base is established on the mobility and degradation of hazardous constituents under field conditions, the sampling schedule should be re-evaluated and modified, if necessary. If hazardous constituents are evident at greater depth than predicted, sampling should be done more frequently. If there is no evidence of movement, sampling may be performed less frequently.

The number of samples to be collected for analysis from each plot is dependent on the expected variability in soil-waste treatment within each plot and on the margin of error that is acceptable for the study, as discussed in Appendix B and in Mason (1983). Information from the reconnaissance study and past analysis of ISS units can be used to help judge the representativeness of field verification plot data. It is estimated that a minimum of three to five samples per plot will be required. Separate sample cores should not be composited before analysis. Composited core samples may not only show a lower variability, but also the true frequency distribution of the raw data may be distorted. Much information may be lost by compositing samples.

The practice of averaging data within a plot may also lead to loss of essential information. Within a plot, where there has been improper application of waste or misjudgment of variability within the plot, averaging results may mask the presence of "hot spots." Data may be presented by using histograms, or any method which illustrates sampling point variance.

6.7.1.2 Soil-Pore Liquid Sample Collection and Analysis--

Percolating water added to the soil by precipitation, irrigation, snowmelt, or waste applications may pass through the treatment zone and rapidly transport some mobile waste constituents or degradation products through the unsaturated zone to the groundwater. Soil-pore liquid monitoring is intended to detect these pulses of contaminants since they may not be observed through the analysis of soil cores.

By monitoring soil-pore liquid, the rate and extent of waste movement through the soil can be determined. If waste is migrating out of the treatment zone, the waste application should be modified and corrective measures taken.

A discussion of types of samplers, installation procedures, and cautions for use are given in the Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units (U.S. EPA 1984b).

6.7.1.3 Soil Pore Liquid Sampler: Vacuum Type--

Vacuum soil-pore liquid samples may be divided into two types (U.S. EPA 1984b): (1) vacuum operated soil-water samplers; and (2) vacuum-pressure samplers. Soil-pore liquid samplers generally consist of a ceramic cup mounted on the end of a small-diameter PVC tube, similar to a tensiometer. The upper end of the PVC tubing projects above the soil surface. A rubber stopper and outlet tubing are inserted into the upper end. Vacuum is applied to the system and soil water moves into the cup. To extract a sample, a small-diameter tube is inserted within the outlet tubing and extended to the base of the cup. The small-diameter tubing is connected to a sample-collection flask. A vacuum is applied via a hand vacuum-pressure pump and the sample is sucked into the collection flask. These units are generally used to sample to depths up to 6 feet from the land surface. consequently, they are used primarily to monitor the near-surface movement of pollutants from the HWLT.

To extract samples from depths greater than the suction lift of water (about 25 feet), a vacuum-pressure lysimeter may be used. These units were developed by Parizek and Lane (1970) for sampling the deep movement of pollutants from a land disposal project. The body tube of the unit is about 2 feet long, holding about 1 liter of sample. Two copper lines are forced through a two-hole rubber stopper sealed into a body tube. One copper line extends to the base of the ceramic cup as shown and the other terminates a short distance below the rubber stopper. The longer line connects to a sample bottle and the shorter line connects to a vacuum-pressure pump. All lines and connections are sealed. In operation, a vacuum is applied to the system (the longer tube to the sample bottle is clamped shut at this time). When sufficient time has been allowed for the unit to fill with solution, the vacuum is released and the clamp on the outlet line is opened. Air pressure is then applied to the system, forcing the sample into the collection flask. A basic problem with this unit is that when air pressure is applied, some of the solution in the cup may be forced back through the cup into the surrounding pore-water system. Consequently, this type of pressure-vacuum system is recommended for depths only up to about 50 feet below land surface. A modification of this type of sampler utilizes a check valve to prevent the liquid being forced out of the cup during application of pressure.

Factors such as rate of water extraction, plugging of the pores of the samplers, and sorption and screening effects by ions can produce as much as 60 percent range in sample concentrations in vacuum type soil pore liquid samplers (Hansen and Harris 1975). Many of these problems may be reduced or eliminated by proper installing of samplers, selection of appropriate samplers, type of vacuum used, and proper sealing of all connections (Parizek and Lane 1970; U.S. EPA 1984b). Vacuum type samplers have been used extensively for studies of the movement of major inorganic cations and anions through the soil profile. The literature is lacking information in the use of vacuum type samplers for organic constituents in soil. Unanswered questions concerning their use include: are organic compounds sampled by these types of devices; are they sorbed or screened by the porous materials; is plugging a problem with oily wastes; and how can volatile organics be sampled without loss in a vacuum system? The Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units (U.S. EPA 1984b) discusses these problems and proposes solutions.

Timing of sampling is critical with these sampling devices, requiring the use of soil moisture measurement devices, such as tensiometers or neutron probes. As the water front moves through the soil profile, the tensiometer or probe will indicate when the wetting front is at the depth of the sampler. Samples should be collected at this time to ensure that the sample is of the water and waste constituents moving through the soil profile and is not stagnant soil-pore water.

6.7.1.4 Pan-Type Soil Pore Liquid Sampler--

Vacuum-type soil liquid samplers, as discussed above, are made of fine porous materials that form a continuum with small soil pores. If water and associated hazardous constituents move uniformly through the small pores of soil matrix as they infiltrate, the movement of hazardous constituents may be readily evaluated using these types of samplers. Water soluble hazardous constituents percolating through soil may, however, bypass much of the total soil mass and thereby would not be collected by porous samplers. The movement of water through large pores, bypassing the smaller pore system has been reported by Kissel et al. (1973), Tyler and Thomas (1977), Quisenberry and Phillips (1976, 1978), Thomas et al. (1978) and Shuford et al. (1977).

The mechanism visualized for water movement through soil is that of a dual-pore soil system. The first set of pores are a continuum of small pores while the second set, often termed macropores, may appear in the form of cracks in shrink-swell clays, as earthworm and old root holes, or as interaggregate pores and interpedal voids (Wagenet et al. 1983; Shaffer et al. 1979). Macropores may be responsible for bulk water and associated hazardous constituents moving through distinct isolated areas of soil with little interaction with the water inside of small pores. Simpson and Cunningham (1982) have shown that rapid flow of wastewater through interpedal cracks may lessen the renovating capacity of the soil because of reduced surface area and contact time. Similarly, because of the rapid flushing of pollutants through large interconnected pores, the movement of such pollutants into finer pores of the soil may be limited. An opposite consequence of macropore flow, as suggested by Thomas and Phillips (1979), is that hazardous constituents in the small pores of surface soil will be bypassed by rapidly moving water and will remain at or near the soil surface.

Macropore flow is of particular importance in well-drained shrink-swell soils with large pores and cracks at high water content. This phenomenon, however, is not limited to such soils but can occur at interfaces between adjacent soil peds (Richie et al. 1972; Thomas and Phillips 1979) and at water contents well below field capacity (Aubertin 1971: Quisenberry and Phillips 1976). At present, there is not sufficient information in the literature defining the soil properties and water regimes where macro-pore flow will occur to the extent that predictions of waste-soil interaction and flow rates based on Darcian theory are grossly incorrect. For this reason, macropore sampling devices should be included in field verification studies.

Macropore sampling devices, consisting of various types of pan samplers, have been described by Shafer et al. (1979), Parizek and Lane (1970), Tyler and Thomas (1977), and U.S. EPA (1984b). The reason for using pan samplers is to confirm whether large quantities of leachate are flowing through structural macropores and possibly bypassing much of the treatment capacity of the soil. Pan samplers collect rapidly moving water because the sampler acts as a textural discontinuity in the soil profile, forming a perched water table above the pan surface. Water then flows through holes in the top surface to be collected and stored in the collection area. This type of flow usually only lasts a few minutes to a few hours after irrigation or a precipitation event occurs (Thomas and Phillips 1979), so samples should be removed within a limited time period (less than 24 hr) to prevent sample quality changes within the pan. The Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units (U.S. EPA 1984b) should be consulted for details on pan-type samplers and installation procedures. The U.S. EPA is presently investigating several new designs of pan samplers.

The number of each type of sampler needed for each field scale plot is dependent on the expected variance in soil-waste treatment within each plot and on the margin of error that is acceptable for the study (Mason 1983). A discussion of this technique is presented in Appendix B. A minimum of two each of vacuum-type and pan-type soil pore liquid samplers is recommended for each field plot.

Barrel lysimeters should have a soil-pore liquid sampler installed at the base of each barrel monolith. Leachate should first be generated in the barrel lysimeters to define background leachate quality. A tracer study should be conducted to evaluate possible sidewall flow and short-circuiting that may bias subsequent soil-pore liquid analysis (Brown et al. 1985).

6.7.2 Groundwater Monitoring

The use of ground water monitoring is not explicitly required in a land treatment demonstration. However, Section 264.272(c)(3)(v) requires consideration of the potential for migration to ground or surface water. At the discretion of the regulatory agency, it may be appropriate to include ground water monitoring in the field verification study design. At a new site without ground water monitoring protection, temporary monitoring wells may be installed adjacent to the field plot area.

6.7.3 Data Interpretation

Field plot studies should be designed to monitor hazardous waste land treatment performance. Data collected from soil core, soil-pore liquid, and groundwater sampling for monitoring purposes may be compared with results of model evaluations. Because of the complex nature of field plot studies and the extreme variance in environmental factors, such as temperature, precipitation, soil properties, etc., quantification of degradation, transformation, and immobilization for prediction of field performance is difficult at the present time. Results of field plot monitoring should demonstrate no movement of hazardous constituents out of the treatment zone. If losses are noted, treatment practices should be modified to prevent continued migration.

Since metal loading limits in soils have been established, the accumulation of metals in the field verification plots should be monitored and compared to those limits shown in Tables 2.4 and 2.5, in order to determine site life based on metal loading rate.

CHAPTER 7

QUALITY ASSURANCE PROGRAM FOR CONDUCTING AN LTD

An integral part of an LTD design is a quality assurance (QA) program to ensure that data collected can be evaluated and interpreted with confidence. An adequate QA program requires that all sources of error associated with each step of the experimental study or monitoring and sampling program be identified and quantified. The most highly developed aspects of QA programs are for laboratory analytical procedures. However, in an LTD, the treatment medium, i.e., the soil, may be extremely non-homogeneous. Soil samples taken only several feet apart my exhibit different soil characteristics or may differ in chemical pollutant concentrations by an order of magnitude. Therefore QA on analytical results is a necessary but not sufficient condition for assessing total sample variability within a soil that is being sampled or used in a laboratory investigation. The analytical errors may account for only a small portion of the total variance (Barth and Mason 1984). High quality soil sampling is required to minimize total variance.

A complete QA program should include sample site selection, sample collection, sample handling, and analysis and interpretation of resulting data. Quality of results obtained are assured in two ways: 1) providing control of various steps in the sampling and analytical processes, from sample collection to data interpretation; and 2) providing adequate replication for statistically determining and quantifying the sources of variation or error in the sampling and analytical processes.

A QA program consists of a system of documented checks which validate the reliability of a data set. It is implemented as a set of basic sampling and measurement procedures and corresponding quality control checks. Necessary elements of a QA program include:

1. Adherence to documented, proven analytical methodology and QC procedures;

2. Performance of sampling and analytical activities by qualified, trained individuals;

3. Maintenance of laboratory physical facilities and sampling equipment;

4. Data recording, handling, storage, and retrieval, including sampling analytical performance parameters, in a scientifically sound manner.

A high quality set of data should include the following measures of sampling and analytical performance:

1. Accuracy - measure of closeness of a measurement to the true value;

2. Precision - measure of the probability that a measurement will fall within certain confidence limits;

3. Sensitivity - a) determination of the method detection limit, which is the lowest concentration of a particular chemical constituent that can be measured reliably in a sample, and b) determination of the limit of detection, which is the lowest concentration level that can be determined to be statistically different from a blank;

4. Representativeness - assurance that the sample being analyzed is a subset of a set and has the average characteristics of the set;

5. Completeness - a data recovery level which will adequately characterize the existing condition that is being monitored.

The QA program for an LTD should include procedures which address the reconnaissance investigation, laboratory analyses and studies, and field plots. If literature data and/or information are used as part of an LTD, an assessment of the representativeness and quality of the information is recommended. Specifically, the QA plan should address:

1. A detailed flow scheme of the work to be performed during the LTD program; individuals responsible for each specific test procedure, including chemical analysis and data interpretation; approximate dates of sampling and analysis.

2. Detailed procedures to ensure the collection of representative soil or waste samples; procedures for a sample receipt log that will include information on storage conditions, sample distribution, and sample identification.

3. A master schedule for tracking all samples through the analytical program. This schedule should include the test performed, individual responsible, and dates of initiation and completion.

4. Standard operating procedures (SOPs) which outline specific details of each test procedure and associated QA/QC requirements.

5. A plan for data handling and interpretation, including data obtained from literature and from laboratory and/or field experiments.

6. A report for each waste used in the LTD that includes the study protocol, a complete set of raw data for each test procedure, the individual(s) generating the data, and the data generating dates.

Information concerning QA/QC procedures and guidance for the preparation of a QA program may be obtained from the following documents:

1. Soil Sampling Quality Assurance User's Guide (Barth and Mason 1984).

2. Methods of Soil Analysis. Part 1: Physical and Mineralogical Properties (Black 1965).

3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories (U.S. EPA 1979a).

4. Test Methods for Evaluating Solid Waste, SW-846 (U.S. EPA 1982b).

5. Methods for Chemical Analysis of Water and Wastes (U.S. EPA 1979b).

6. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry" (ACS 1980).

7. "Elements of a Laboratory Quality Assurance Program" (Dressman 1982).

8. Guidelines for Quality Assurance/Quality Control Program (U.S. EPA 1980).

9. User's Guide to the Contract Laboratory Program (U.S. EPA 1984c).

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Appendix A

SUMMARY OF TREATMENT DEMONSTRATION PERMIT APPLICATION INFORMATION REQUIREMENTS (U.S. EPA 1984a)

I. Treatment Demonstration Plan

  A. Wastes for treatment demonstration plan

    1. List of all wastes (hazardous and nonhazardous) included in the treatment demonstration

      a. Common name and EPA hazardous waste ID number
      b. Generating process
      c. Expected monthly quantity
      d. Form of waste and approximate moisture content

    2. List all potentially hazardous constituents (Appendix VIII) and pertinent nonhazardous constituents in wastes listed in I.A.

    3. Quantitative analysis of each waste listed in I.A.

      a. Concentration of each hazardous constituent listed in I.B. based on boiling point ranges (25°C, 25 to 105°C, 105 to 250°C, and > 250°C)
      b. Percent water content
      c. Specific gravity or bulk density
      d. pH
      e. Electrical conductivity
      f. Total acidity or alkalinity
      g. Total organic carbon

  B. Data sources of treatment demonstration

    1. Identify information sources for data used in treatment demonstration

    2. Description of data from each source and how data are to be used in treatment demonstration

  C. Laboratory and field test design

    1. Laboratory tests

      a. Name of test
      b. Objective of test

   - c. Step-by-step materials and methods
   - d. Schedule of completion
   - e. List of full scale operating characteristics that are or are not simulated in test
   - f. List of data to be obtained in test along with final form of of data presentation

2. Field tests

   - a. Objective of test
   - b. Scale drawing showing location of test plots with respect to proposed land treatment unit
   - c. Number and size of test plots
   - d. Horizontal and vertical dimensions of the treatment zone
   - e. Statistical design of test
   - f. Preparation activities for test plot(s)
   - g. Waste application rate on each plot
   - h. Irrigation method and scheduling
   - i Methods for establishing and maintaining vegetation if applicable
   - j. Methods for monitoring and recording daily meteorological data
   - k. Monitoring procedures for: soil, soil-pore liquid, surface runoff, vegetation, groundwater, and air as applicable
   - l. Daily schedule of events and activities
   - m. Rationale for design and management of field tests to preclude hazardous constituent migration to ground or surface waters
   - n. List of data to be obtained in test along with final form of data presentation
   - o. Clean-up procedures upon completion of field tests

II. Treatment Demonstration Results

A. Wastes and waste composition

Information regarding wastes different from those specified in Treatment Demonstration Plan using criteria of I.A. above. Include pretreatment or mixing activities utilized.

B. Degradation/transformation

Information on rate and extent of degradation/transformation of specific hazardous constituents as well as bulk organic fraction of waste(s).

1. Existing literature data

   - a. Brief written review of scientific literature and previous studies
   - b. Documentation of sources of information in text and bibliography

c. Description of test procedures and results as per II.B.3 or II.B.4 as appropriate

2. Operating data

   a. Description of existing facility, operating records, waste composition, waste application rate(s), and data demonstrating degradation of hazardous constituents and/or bulk organics
   b. At minimum provide analytical results of soil sampling for hazardous constituents and plot percent degradation or transformation as a function of time for each waste application treatment

3. Laboratory test results

   a. Name of test
   b. Test procedures including laboratory apparatus, experimental design, waste application rate(s), preparation and handling of soil and waste(s), analytical methods, sampling procedures, and all test conditions
   c. Test results including tables and/or graphs specific to the test method utilized, along with the half-life of each organic hazardous constituent calculated from experimental data
   d. Discussion and interpretation of results

4. Field test results

   a. Field test objectives
   b. Field test procedures used including physical plot characteristics, soil and waste properties, etc., and any and all changes from procedures described in the Treatment Demonstration Plan
   c. Field test results in form of tables and graphs to demonstrate degradation or transformation of organic hazardous constituents. Include analytical results, plot of percent degradation/transformation versus time, half-life of hazardous constituents in the treatment zone, and application rate providing optimal treatment performance.

C. Immobilization

Information on potential for organic and inorganic hazardous constituents to migrate from treatment zone under typical waste application rates and operating conditions.

1. Existing literature data

   a. Brief written review of scientific literature and previous studies

   b. Documentation of sources of information in text and bibliography
   c. Description of test procedures and results as per II.C.3 below

2. Operating data

   a. Description of existing facility, operating records, waste composition, waste application rate(s), and data reflecting the mobility of hazardous constituents
   b. Sampling procedures and analytical methods should be included with monitoring data presented in detail described in II.C.4 below

3. Laboratory test results

   a. Name of test
   b. Test objectives
   c. Test procedures including laboratory apparatus, experimental design, waste application rate(s), preparation and handling of soil and waste(s), analytical methods, sampling procedures, and all test conditions
   d. Test results including tables and/or graphs specific to the test method utilized
   e. Discussion and interpretation of results

4. Field test results

   a. Field test objectives
   b. Field test procedures including physical plot characteristics, soil and waste properties, etc., and any and all modifications from procedures described in the Treatment Demonstration Plan
   c. Field test results in the form of tables and graphs to demonstrate the rate and extent of hazardous constituent migration during the field test

D. Volatilization

Information on potential for volatilization of hazardous constituents from the treatment zone which is not considered degradation, transformation nor immobilization. Extensive quantitative information is not required if it can be shown that volatilization will not be a significant release mechanism for the hazardous constituent of concern.

1. Existing literature data

   a. Brief written review of scientific literature and previous studies

   b. Present results as vapor pressure (mm Hg), and estimated flux (mass/area) versus time, along with other pertinent values as appropriate
   c. Document sources of information in text and bibliography

2. Operating data

   a. Description of existing facility, operating records, waste composition, waste application rate(s), and data reflecting volatilization potential of hazardous constituents
   b. Description of sampling procedures and analytical methods along with monitoring data

3. Laboratory test results

   a. Name of test
   b. Test procedures including laboratory apparatus, experimental design, waste application rate(s), analytical methods, sampling procedures, and all test conditions
   c. Test results including graph showing mass of hazardous constituent volatilized per unit area as a function of time for various application rates
   d. Discussion and interpretation of results

4. Field test results

   a. Field test objectives
   b. Field test procedures including physical plot characteristics, soil and waste properties, etc., and any and all modifications from procedures described in the Treatment Demonstration Plan
   c. Field test results in form of tables and graphs to demonstrate the flux of hazardous constituents (mass/area) as a function of time for various application rates

E. Microbial toxicity

Information on toxicity of applied waste to soil microorganisms to ensure maintenance of biodegradation within the treatment zone.

1. Existing literature data

   a. Brief written review of scientific literature and previous studies
   b. Document source of information in text and bibliography

2. Operating data

   a. Description of existing facility, operating records, waste composition, waste application rate(s), and data showing relative microbial activity as a function of time for various concentrations of waste in the soil

        b. Sampling procedures and analytical methods along with monitoring data

    3. Laboratory test results

        a. Name of test
        b. Test procedures including laboratory apparatus, experimental design, waste application rate(s), analytical methods, sampling procedures, and all test conditions
        c. Test results including tables or graphs that show relative microbial activity as a function of time for various concentrations of waste in soil
        d. Discussion and interpretation of results

    4. Field test results

        a. Field test objectives
        b. Field test procedures including physical plot characteristics, soil and waste properties, etc., and any and all modifications from procedures described in the Treatment Demonstration Plan
        c. Field test results in the form of tables and graphs that demonstrate relative microbial activity as a function of time at various waste application rates or operating conditions

F. Phytotoxicity

Information on phytotoxicity of nonbiodegradable hazardous constituents immobilized in the treatment zone or vegetative cover during the operating life of the facility to planned cover crop following closure of land treatment facility.

1. Existing literature data

    a. Brief written review of scientific literature and previous studies
    b. Document source of information in text and bibliography
    c. Include information such as plant species, waste application rates, and test procedures

2. Operating data

    a. Description of existing facility, operating records, waste application rate(s), and data showing the toxicity of the waste
    b. Sampling procedures and analytical methods along with monitoring data

3. Laboratory test results

    a. Test procedures including apparatus, experimental design, waste application rate(s), waste application schedule, and plant varieties

   b. Test results should show the concentration of waste in the soil that causes a specified decrease in plant growth

4. Field test results

   a. Field test objectives
   b. Field test procedures including physical plot characteristics, soil and waste properties, etc., and any and all modifications from procedures described in the Treatment Demonstration Plan
   c. Field test results in the form of tables or graphs that demonstrate the concentration of waste and waste constituents that cause a specified decrease in plant growth or survival
   d. Discussion and interpretation of results

APPENDIX B

STATISTICAL CONSIDERATIONS FOR THE PERFORMANCE OF AN LTD

INTRODUCTION

The information obtained in aN LTD should be representative of the soil and soil/waste system if it is to be useful, for the results may have profound health and economic consequences. The sampling designs used should provide information of maximum reliability and minimum cost. Statistical plans, including knowledge of the expected variability and confidence limits of analytical methods used, sampling designs employed, and data interpretation procedures used, must be incorporated into the LTD from the beginning. It is highly recommended that the applicant secure the services of a statistician familiar with the design of sampling and monitoring studies to prepare the sampling design plan for the reconnaissance investigation.

Statistics are required when data are collected and analyzed to make judgments about some population attribute. Statistical analyses may be used to estimate some overall property (e.g. mean value of hydraulic conductivity, concentration of a waste constituent, etc.), the pattern of distribution (e.g. soil pH distribution over a field), for comparison purposes (e.g., testing mean differences of treatment versus background), and in experimental design (e.g., study of degradation rates over time). Two critical problems in statistical design are the assurance of the collection of a representative sample and the ability to make accurate inferences from the sample data to the population.

COLLECTION OF REPRESENTATIVE SAMPLES

One of the key characteristics of a soil system that should be recognized by the applicant is the extreme variability in soil properties (Mason 1983). Mason summarizes available information on soil variability as expressed by the coefficient of variation in the following manner:

> Coefficients of variation for soil parameters have been reported ranging from as low as 1 to 2 percent to as high as 850 percent. White and Hakonson (1979), for example, noted that the CV for plutonium in the soils of a number of test sites ranged from 62 percent to 840 percent. Mathur and Sanderson (1978) reported coefficients for natural soil constituents (i.e., part of the soil itself) varying from 5.6% to 75.2%. Harrison (1979) evaluated four phosphorus properties of soil and reported CV values ranging from 11

percent to 144 percent with the highest values being for available P. Hindin et al. (1966) reported a CV of 156% for insecticide residue concentrations in a square block of soil that was 30 inches on a side.

Mausbach et al. (1980) reported on a study conducted by the Soil Conservation Service (SCS) laboratory in Lincoln, Nebraska. Matched pairs of samples were collected from areas within a soil series. The samples were stratified by a number of factors in order to reduce the variability. The samples were collected from the modal phase of the series and were collected at distances that ranged from 2 to 32 km from the other members of the pair. The authors note that the literature indicates that up to half of the variability may occur within a distance of one meter. (Studies are now underway at Lincoln to determine variability within this one meter distance.) Mausbach et al. (1980) reported that in their study of the variability within a soil type, the CVs for physical properties ranged from 9 to 40% for loess, 23 to 35% for glacial drift, 33 to 47% for alluvium and residuum, 18 to 32% for the A and B horizons, and 33 to 51% for the C horizons. The CVs for the chemical properties tended to be higher, ranging from 12 to 50% for Alfisols, 4 to 71% for Aridisols, 6 to 61% for Entisols, 10 to 63% for Inceptisols, 9 to 46% for Mollisols, 16 to 132% for Spodosols, 10 to 100% for Ultisols, and 8 to 46% for Vertisols.

This soil variation must be taken into consideration during the design of a sampling and surveying plan. A single sample or a single composite sample will not provide information on the types of pollutants present nor the routes of migration of the pollutants. Compositing assumes that the soil or soil/waste system being investigated is virtually homogeneous and therefore the number of analyses required and the associated costs can be reduced. Compositing obscures variability in a measurement, and information about this important property of the population will be lost. Statistical technologies designed to account for variation must be included in any soil characterization study. The sample arithmetic mean may be used as an estimate of central tendency, while the variance (or its square root value, the standard deviation) may be used to measure variability.

In situations where little is known about the distribution of a population parameter, nonparametric tests and evaluations are used to make inferences. If enough is known about a parameter to indicate that its behavior can be approximated by a parametric model such as a normal, log normal, or Poisson distribution, the use of parametric models is preferable. In particular, the theoretical normal distribution has been well described and its properties have been extensively tabulated. Making inferences is relatively straightforward if normality can be assumed. Many naturally occurring linear variables are well approximated by this distribution. For many other environmental variables, a transformation of data using a square-root or logarithmic transformation, will yield an approximately normal distribution. Examples of soil parameters following the normal and log normal distribution are shown in Table B.1.

Table B.1 Frequency Distribution of Soil Properties (Rao et al. 1979, Barth and Mason, 1984).

Soil Property	Type of Frequency Distribution
Bulk Density	Normal
Organic Matter Content	Normal
Clay Content	Normal
Soil-Water Content at a Given Tension	Normal
Air Permeability	Log normal
Saturated Hydraulic Conductivity	Log normal
Soil-Water Flux	Log normal
Pore-Water Velocity	Log normal
Solute Dispersion Coefficients	Log normal

Even if a distribution is itself nonnormal, the sample averages from such a population are often normally distributed. The student-t test relies on this basic Central Limit theorem to allow comparison of mean sample differences from nonnormal populations. Finally, the robustness of tests using the normal distribution can handle moderate departures from normality.

An important consideration is whether or not a given variable under study is distributed randomly or nonrandomly. Use of normal approximations presupposes a random variable, that is, a variable whose individual sample values are defined only by their probability of occurrence. Individual sample values are independent of one another. By contrast, values from a nonrandom variable taken close together in time or space will exhibit relatedness or covariation. Many environmental variables will contain both a random and nonrandom component.

SAMPLING DESIGNS

Four basic statistical sampling designs may be used in soil studies: simple random, stratified random, systematic, and judgmental sampling. Complete explanations of each of these designs are presented in Preparation of Soil Sampling Protocol: Techniques and Strategies (Mason 1983). The type of sampling design chosen for the reconnaissance investigation should be reported to the permit writer and included in the permit application.

A random sample is any sample in which the probabilities of selection are equal and independent of the other members that comprise the population. Random samples are selected by some method that uses chance as the determining factor of selection. In simple random sampling of soils, the chances of selection of any particular segment of the soil system must be the same, i.e., each member of the soil population must have an equal probability for selection. A random location sampling plan is appropriate if the parameter distribution is itself expected to be random. Simple random sampling may not give the desired precision because of the large statistical variations encountered in soil sampling. Therefore one of the other designs may be more useful.

The number of samples necessary to attain required information may be reduced by the use of stratified random sampling. The sampling area is divided into smaller, more homogeneous subareas called strata. These strata are defined by some identifiable boundary that is based on topography, soil chemical or physical properties, or some stratigraphic feature. This is the technique most likely to be used in the analysis of waste distribution in the soils at a land treatment unit, since the definition of "uniform areas" is required at the site for further sampling efforts and study. The use of uniform areas should lead to increased precision if the subareas selected are more homogeneous than the total population. Within a uniform area, sampling is conducted as with the simple random sampling.

The systematic sampling plan provides better coverage of the soil study area than does the simple random sample when spatial variability is expected. Samples are collected in a regular pattern (usually a grid or line transect) over the areas under investigation. The starting point is located by some random process, then all other samples are collected at regular intervals in one or more directions. The orientation of the grid lines should also be randomly selected.

Judgmental sampling is usually used in conjunction with one of the other methods in order to include areas of unusual patterns, (e.g., pollutant "hot spots"). However, when used by itself, this approach is subject to bias and may lead to faulty conclusions. If judgmental sampling is used, duplicate or triplicate samples should be taken to increase the level of precision. Data from judgmental sampling areas should be identified.

NUMBER OF SAMPLES

A larger number of samples usually results in a better estimate of properties of a population. However, the cost of sampling and analysis also must be considered in sample design. In the performance of an LTD, which requires sample measurements for many constituents and properties of wastes, soils, soil-pore liquid, and groundwater, techniques to minimize sample numbers should be employed.

For many types of random variables, the t-statistic is used to estimate confidence levels of the true population mean for small sample sizes; similar techniques are used to estimate the population variance. In general, the smaller the sample, the wider is the confidence interval in which a population mean is expected to lie for a given probable level of confidence. For certain comparisons in experimental studies, it is necessary to reduce the confidence interval (i.e., increase confidence) in order to evaluate the reliability of the results. Generally, the confidence level is controlled through choice of an appropriate sample size.

To determine the number of samples required, the use of a statistical procedure incorporating the estimated variability of concentrations or levels of soil or waste constituents of interest, the desired level of confidence of the data, and a specified level of precision (or allowable margin of error to be met by the results) is recommended. One such procedure is described in Preparation of Soil Sampling Protocol: Techniques and Strategies (Mason 1983). Further information on the use of this technique as well as tabular solutions to required statistical formulas are given in Soil Sampling Quality Assurance User's Guide (Barth and Mason 1984).

Mason (1983) describes the statistical technique in the following manner:

> If an estimate of the variance can be obtained from either a preliminary experiment, a pilot study, or from the literature, the number of samples required to obtain a given precision with a specific confidence level can be obtained from the following equation:
>
> $$n = t^2{}_\alpha s^2/D_2$$
>
> where D is the precision given in the specifications of the study, s^2 is the sample variance, and t is the two-tailed t-value obtained from the standard statistical tables at the α level of significance and (n-1) degrees of freedom. D is usually expressed as + or - a specified number of concentration units (i.e., + or - 5.00 ppm). The equation can also be written in terms of the coefficient of variation (CV) as follows:
>
> $$n = (CV)^2 t^2 \alpha/p^2$$
>
> where CV is the coefficient of variation, p is the allowable margin of error expressed as a percentage (D/y), and y is the mean of the samples.
>
> The margin of error is needed in determining the number of samples required to meet the precision specified. This is often expressed as the percentage error that the scientist is willing to accept or it may be the difference that he hopes to detect via the study. The margin of error chosen is combined with the confidence level to derive an estimate of the number of samples required. The smaller the margin of error, the larger the number of samples required.

As the variability increases in a measurement, the ability to detect differences in constituent concentration decreases.

The reliability of data is expressed by the confidence level, which states the level of precision of the results generated by the study. Mason (1983) explains confidence levels as follows:

> Three confidence levels are normally used by the scientific community. These are usually expressed as + or - 1 standard deviation, + or - 1.96 standard deviations, and + or - 2.58 standard deviations, which covers 68%, 95%, and 99% of the total

population respectively. Another way to state this is to say that the probability is 0.32 (or 1 in 3) that the value is outside of one standard deviation on either side of the mean; 0.05 (or 1 in 20) that the value is outside of 1.96 standard deviations; or 0.01 (or 1 in 100) that the value is outside of 2.58 standard deviations.

The first step in the use of this statistical procedure in the reconnaissance investigation is an initial determination of the variability of concentrations or levels of hazardous waste or soil constituents. Provost (1984) recommends that for such an exploratory study, 6-15 samples per uniform area should be sufficient. Realizing that the cost of analyses of hazardous constituents may be quite high, a possible method to evaluate the variance of waste distribution in soil is to use a surrogate waste parameter which is easier and less expensive to analyze than hazardous waste constituents (e.g., oil and grease for petroleum refinery wastes). A large variability in concentrations of this surrogate parameter may mean that a larger number of samples will be required to adequately describe the distribution and concentrations of wastes at the site. Therefore, a well-managed and properly designed site that has had uniform waste application and has avoided the formation of "hot spots" due to uneven waste application or runoff will require a fewer number of samples than a site that has been less well-managed. The number of samples required during long-term monitoring of an existing site may also be affected by the variability of waste distribution determined during the reconnaissance investigation. Examples of the number of samples required using this statistical procedure is given in Table B.2.

The use of this statistical method assumes that the measurements are independent of one another and are distributed normally (Barth and Mason 1984). If one or the other, or both, of these assumptions is not valid, undetermined errors may be introduced. If the normal distribution is not valid, an assumption of a log normal distribution may be considered. Table B.1 listed those soil properties which are known to be usually normally or log normally distributed. In general, a variable whose variance increases in direct proportion to its mean value (especially over a few orders of magnitude), is best described by a log normal distribution. If the measurements are dependent on one another, it may be possible to replace classical statistical techniques with kriging. Examination of the data collected from the exploratory study should enable the statistician to decide on an appropriate statistical technique.

The distribution pattern of chemical constituents of soil including pollutants is truncated at zero. This characteristic often gives rise to a frequency curve skewed to the low end of the concentration scale. When this situation is encountered, the data can usually be transformed to a normal distribution by taking the log of the data. Alternatively, a statistician may be consulted for preparation of a procedure appropriate for determining sample numbers for constituents which have random, log normal distribution.

It is recognized that the cost of analysis for hazardous waste constituents in soil cores divided into segments may be extremely expensive. The more

Table B.2 Examples of Number of Samples Required to Achieve a Specified Analytical Precision and Level of Confidence, Based on Expected Variability of Sample Concentrations, as Determined in an Exploratory Study

Coefficient of Variation (measured)	Confidence Level (specified)	Level of Precision (Specified) 10%	50%	100%
		Number of Samples Required		
1	95	2	1	1
	90	1	1	1
	70	1	1	1
	50	1	1	1
4	95	3	1	1
	90	2	1	1
	70	1	1	1
	50	1	1	1
10	95	6	2	2
	90	5	2	1
	70	2	1	1
	50	1	1	1
50	95	99	6	3
	90	70	5	2
	70	28	2	1
	50	12	1	1
100	95	385	18	6
	90	271	13	3
	70	115	6	2
	50	47	3	1

important data from the soil cores are the concentrations of constituents at and just below the bottom of the treatment zone (to determine if waste constituents are migrating out of the treatment zone) and in the zone of incorporation (ZOI) (to determine if waste constituents are accumulating in the ZOI). The permit writer may use discretion in allowing the compositing of samples from the same depths between the ZOI and the bottom of the treatment zone from soil cores within the same uniform area if the variance determined by the analysis of the surrogate parameter is not too large.

If the variance found during the exploratory study is so great as to require such a large number of samples that the cost is prohibitive, or there is a lack of available laboratory capacity to handle the analyses, the permit writer may specify a lower level of confidence and/or a lower level of precision for the data. The permit writer should use caution to prevent cost from becoming the excuse for failing to apply statistical criteria in the design of the reconnaissance program. Environmental sampling usually attempts to attain a level of 95 percent confidence. However, lower levels may be accepted as long as the level is known and agreed upon before the study is started. Use of the tables given in Appendix A of the Soil Sampling Quality Assurance User's Guide (Barth and Mason, 1984) may be used to estimate the number of samples required using different specified levels of confidence and degrees of precision. The data from the reconnaissance investigation are used to determine whether additional laboratory and/or field studies are required to complete the LTD. For such conclusions to be drawn, there is a definite need to measure the reliability of the data. In general, any approach for collecting LTD data without adequate quality assurance/quality control (QA/QC) and statistical planning should be strongly discouraged (Barth and Mason 1984).

STATISTICAL INFERENCES

Estimation

All of the possible soil cores in a land treatment demonstration plot and all of the soil pore water at the bottom of the treatment zone are examples of populations from which samples may be drawn in a hazardous waste land treatment demonstration. Given analytical results from random samples from such a population, appropriate statistical techniques should be used to report the analyses and provide information about the data's representativeness of the population from which the samples were drawn.

In every case the sample mean (average) should be reported along with the sample variance, standard deviation, or coefficient of variation. In most situations, the mean is the best single number to represent the population. A confidence interval for the mean should be calculated and reported. The confidence interval is a statement of confidence (e.g., 95 percent confident) by the person reporting the data that the population mean lies between the upper and lower limits of the interval. If the population data is normally distributed or the transformed data is normally distributed (e.g., log normal data), the calculation of the confidence interval uses the student's t statistic. Similar confidence intervals for the variance of a normal population are less frequently reported, but may be calculated using the chi-squared (χ^2) statistic. If the population data are far from normally distributed and cannot be transformed to be approximately normal, a statistician familiar with exact and nonparametric statistical procedures should be consulted.

In situations where single measurements may need to be evaluated as indications of increasing hazardous constituent concentration, the upper tolerance limit for the background (existing) concentration should be calculated. The tolerance limit is based on the mean value of the constituent in the uniform area or plot to be used for demonstration. Subsequent data from a sample that exceeds the tolerance limit indicates a change in the population and would justify a more intense investigation if the result occurred at a critical point in the treatment scheme (e.g., below the treatment zone).

Formulae and tabulated statistical values for calculating all the above statistics can be found in most introductory statistics texts.

Hypothesis Testing

Statistics for determining the significance of changes in sample mean or variance values fall generally in the category of hypothesis testing. As an example, one might hypothesize that the population mean of a waste constituent is currently equal to the mean at the last sampling time. The alternate hypothesis would be that the means are not equal. The alternate hypothesis could state that the mean has increased or decreased.

Where single pairs of means from normal populations are being compared, the use of student's t-test is recommended. Care should be taken to apply either the two-tailed or one-tailed test appropriately, depending on the nature of the hypotheses.

Where more than one comparison of experimental treatment effects is to be made, the use of analysis of variance (ANOVA) procedures is recommended. If ANOVA results indicate significant differences exist among the treatments, tests for multiple comparisons between means such as Duncan's multiple range test or Tukey's honestly significant difference test should be used to identify means that are significantly different from one another.

Procedures for performing the above tests are described in most introductory textbooks and are available in many computer software statistical packages.

APPENDIX C
INFORMATION CONCERNING THE HWLT MATHEMATICAL MODEL

C.1 DETAILED DESCRIPTION OF MODEL EQUATIONS

Basic Equation

A constituent of interest may exist simultaneously in more than one phase. The strategy adopted for land treatment facility description is to derive the basic differential equation for a single constituent in a single phase, and then construct a system of equations as necessary to describe more complex relationships. A mass balance must include terms for the following mechanisms:

$$\begin{aligned}
\underset{\text{I}}{\begin{pmatrix}\text{Rate change in mass}\\ \text{of constituent in}\\ \text{control volume}\end{pmatrix}} &= \underset{\text{II}}{\begin{pmatrix}\text{mass flux due to}\\ \text{dispersion within}\\ \text{the phase}\end{pmatrix}} + \underset{\text{III}}{\begin{pmatrix}\text{mass flux due to}\\ \text{diffusion within}\\ \text{the phase}\end{pmatrix}}\\
&+ \underset{\text{IV}}{\begin{pmatrix}\text{mass flux due to}\\ \text{advection to}\\ \text{the phase}\end{pmatrix}} - \underset{\text{V}}{\begin{pmatrix}\text{mass decay rate}\\ \text{within}\\ \text{the phase}\end{pmatrix}}\\
&+ \underset{\text{VI}}{\begin{pmatrix}\text{mass supply rate}\\ \text{into the phase}\end{pmatrix}} \pm \underset{\text{VII}}{\begin{pmatrix}\text{mass transfer}\\ \text{rate among}\\ \text{phases}\end{pmatrix}} \qquad \text{(C1.1)}
\end{aligned}$$

For a phase partially filling a control volume of dimension A by dz, the terms in Equation C1.1 may be expressed mathematically by:

$$\frac{\partial C\Theta A dz}{\partial t} = \frac{\partial \Theta A^{\delta} \cdot \frac{\partial c}{\partial z}}{\partial z} dz + \frac{\partial \Theta A^{\xi} \cdot \frac{\partial c}{\partial z}}{\partial z} dz + \frac{\partial(-V\Theta AC)}{\partial z} dz - \mu C\Theta A dz + \psi S A dz + \quad A dz \qquad \text{(C 1.2)}$$

where:

C = concentration, $\dfrac{\text{g constituent}}{\text{m}^3\text{ phase}}$,

Θ = control volume phase content, $\left(\dfrac{\text{m}^3\text{ phase}}{\text{m}^3\text{ control volume}}\right)$,

A = horizontal area of control volume, (m^2),

z = depth, positive downward, (m),

t = time, (days),

δ = dispersion coefficient related to movement the of phase, (m^2/day),

ξ = diffusion coefficient for the constituent in quiescent phase, (m^2/day),

V = vertical pore velocity of the phase in the soil, (m/day),

μ = first order decay rate, (1/day),

S = supply rate of the constituent into the control volume,(g/m^3 control volume/day),

ψ = mass adsorption rate into the control volume, (g/m^2 control volume/day), and

dz = depth of the control volume, (m).

Equations by Jury (1983) and Short (1985)

Equation C1.2 may be simplified by assuming:

1. Θ is constant with time.
2. A is set equal to $1m^2$, i.e., applies to a 1 m^2 soil column, and
3. Θ, D, ξ, and V are constant with depth.

this results in:

$$\Theta\frac{\partial C}{\partial t} = \Theta D\frac{\partial^2 C}{\partial z^2} - \Theta V\frac{\partial C}{\partial z} - \mu\Theta C + S + \Psi \tag{C1.3}$$

where:

D = total dispersion coefficient (m^2/day), equal to $\partial + \xi$.

The following additional assumptions were used by Jury et al. (1983) and Short (1985):

1. Only four phases exist in the soil environment: water, oil, air, and soil grains, and
2. The mass transfer rates among phases are instantaneous and progress to the extent necessary to reach equilibrium.

These assumptions greatly reduce the complexity of the system equations because the constituent states are in equilibrium at all times. Because equilibrium is assumed at all times, the mass transfer rate, ψ may be eliminated from the equations by introducing an algebraic constraint describing isotherm equilibrium partitioning.

Applying Equation C1.3 to each of the four phases in a control volume (Figure 4.2) results in:

$$\Theta_w \frac{\partial C_w}{\partial t} = \Theta_w D_w \frac{\partial^2 C_w}{\partial z^2} - \Theta_w V_w \frac{\partial C_w}{\partial z} - \Theta_w \mu_w C_w + S_w \qquad \text{(for water)} \qquad \text{(C1.4a)}$$

$$\Theta_o \frac{\partial C_o}{\partial t} = \Theta_o D_o \frac{\partial^2 C_o}{\partial z^2} - \Theta_o V_o \frac{\partial C_o}{\partial z} - \Theta_o \mu_o C_o + S_o \qquad \text{(for oil)} \qquad \text{(C4.1b)}$$

$$\Theta_a \frac{\partial C_a}{\partial t} = \Theta_a D_a \frac{\partial^2 C_a}{\partial z^2} - \Theta_a V_a \frac{\partial C_a}{\partial} - \Theta_a \mu_a C_a \qquad \text{(for air)} \qquad \text{(C4.1c)}$$

$$\rho \frac{\partial C_s}{\partial t} = -\rho \mu_s C_s \qquad \text{(for soil)} \qquad \text{(C4.1d)}$$

where:

w, o, a, and s= subscripts identifying water, oil, air, and soil grain phases, respectively,

C_w= concentration in water, (g/m^3 water),

C_o= concentration in oily waste, (g/m^3 oil),

C_a= concentration in air, (g/m^3 air),

C_s= adsorbed mass on soil grains, (g constituent/g soil grains), and

ρ= bulk density of soil, (g soil grains/m^3 control volume).

The sum of the masses in each phase equals the total mass in the control volume, C_T, (g/m^3 control volume), i.e.,

$$C_T = \Theta_w C_w + \Theta_o C_o + \Theta_a C_a + \rho C_s \qquad \text{(C1.5)}$$

Summing equations C1.4a through C1.4d and substituting Equation C1.5 yields:

$$\frac{\partial C_T}{\partial t} = \Theta_w D_w \frac{\partial^2 C_w}{\partial z^2} + \Theta_o D_o \frac{\partial C_o}{\partial z} + \Theta_a D_a \frac{\partial^2 C_a}{\partial z^2} - \Theta_w V_w \frac{\partial C_w}{\partial z} - \Theta_o V_o \frac{\partial C_o}{\partial z} - \Theta_a V_a \frac{\partial C_a}{\partial z}$$
$$- \Theta_w \mu_w C_w - \Theta_o \mu_o C_o - \Theta_a \mu_a C_a - \rho \mu_s C_s + S_w + S_o \qquad \text{(C1.6)}$$

Based on assumptions made above, C_w, C_o, C_a, and C_s are at equilibrium at all times, and the concentrations in all phases can be expressed in terms of the concentration in one of the phases. With the further assumption that equilibrium conditions can be expressed by linear isotherms, the following relationships between phase concentrations results:

$$C_o = K_{ow} C_w$$
$$C_a = K_{aw} C_w$$
$$C_s = K_{sw} C_w$$

and

$$C_w = K_{wo} C_o$$

$$C_a = K_{ao}C_o$$
$$C_s = K_{so}C_o$$

and

$$C_w = K_{wa}C_a$$
$$C_o = K_{oa}C_a$$
$$C_s = K_{sa}C_a$$

and

$$C_w = K_{ws}C_s$$
$$C_o = K_{so}C_s$$
$$C_a = K_{as}C_s$$

It should be observed that only three of the coefficients are independent. For example:

$$C_o = K_{ow}C_w = K_{oa}C_a = K_{oa}(K_{aw}C_w),$$

therefore, $K_{ow} = K_{oa}K_{aw}$.

In order to conform with the equation developments presented by Jury (1983) and Short (1985), partitioning coefficients for the dissolved state in water can be used as follows:

$$C_T = B_wC_w = B_oC_o = B_aC_a = B_sC_s \qquad \text{(C1.7)}$$

where:

$$B_w = \Theta_w + \Theta_oK_{ow} + \Theta_aK_{aw} + \rho K_{sw}$$
$$B_o = (\Theta_w/K_{ow}) + \Theta_o + (\Theta_aK_{aw}/K_{ow}) + (\rho K_{sw}/K_{ow})$$
$$B_a = (\Theta_w/K_{aw} + (\Theta_oK_{ow}/K_{aw}) + \Theta_a + (\rho K_{sw}/K_{aw})$$
$$B_s = (\Theta_w/K_{sw}) = (\Theta_oK_{ow}/K_{sw}) + (\Theta_aK_{aw}/K_{sw}) + \rho$$

Now Equation C1.6 can be written as:

$$\frac{\partial C_T}{\partial t} = D_E\,\frac{\partial^2 C_T}{\partial z^2} - V_E\,\frac{\partial C_T}{\partial z} - \mu E C_T + S_E \qquad \text{(C1.8)}$$

where:

$$D_E = (D_w\Theta_w/B_w) + (D_o\Theta_o/B_o) + (D_a\Theta_a/B_a)$$
$$V_E = (V_w\Theta_w/B_w) + (V_o\Theta_o/B_o) + (V_a\Theta_a/B_a)$$
$$\mu_E = (\mu_w\Theta_w/B_w) + (\mu_o\Theta_o/B_o) + (\mu_a\Theta_a/B_a) + (\mu_s\,\rho/B_s)$$

S_E = Total loading to control volume, (g/m^2 surface area/day/m depth).

Jury et al. (1983) exclude the oil medium ($\Theta_o = 0$) and the supply-rate ($S_E = 0$), and solve Equation C1.8 for the following boundary and initial conditions:

Initial conditions

$$C_T(z,t=o) = C_{T_0} \quad 0 < z < L \text{ for } t = o$$

$C_{T(z,t=o)} = 0 \quad L < z \quad \text{for } t = o$

Boundary conditions

$C_{T(z=\infty,t)} = 0$

$-D_E \frac{\partial C_T}{\partial z} + V_E C_T = -H_E C_T \quad \text{for } z = o$

where:

C_T = initial mass concentration in the plow zone, (g/m^3),
L = depth of plow zone, (m), and
H_E = upper boundary effective mass transfer coefficient.

Short (1985, 1986) retained the oil medium in the plow zone and allowed it to decay at a first order rate. He used the empirical relationships developed by Clapp and Hornberger (1978) to estimate the pore velocity of the water based on the recharge rate and the soil characteristics. Dispersion was neglected in the water medium.

The program listed in Appendix F solves the system of Equations C1.4a through C1.4d except that dispersion is neglected in the water and oil phases, and advection is neglected in the air and oil phases. Linear isotherms are used to partition the constituent among the phases to provide local equilibrium through time.

C.2 USER INFORMATION

Figure C2.1 is a sample of an input data file. The first 15 characters in each row may be used for comments by the user and are treated as text. In Figure C2.1 these comments are used to identify the coefficients which are input in the respective rows. The remaining space on each row is used to enter data. Each data value must contain a decimal point and values must be separated by commas. The first six rows contain program control information as indicated below:

Row 1. Title NAPHTHALENE, Application 4 times per year.

Row 2. DTZON = Depth of treatment zone, (m), DPZON = Depth of Plow Zone, (m).

Row 3. DETECT DZ = Depth increment, (m).

Row 4. TOTAL TIME = Length of run, (days), DT = Time increment, (days).

Row 5. TOI = The time (days) into a run that a new output interval is set.

Row 6. DTOI = The new output interval, (days).

Row 7. Contains soil characteristics
SMLB = Soil Moisture Coefficient, PHI = Soil Porosity (cm^3/cm), and ROES = Bulk Density (g/cm^3).

Row 8. Contains water phase characteristics
RMUWPZ = Constituent Degradation Rate within water in Plow Zone,(1/day), and UWLZ = Constituent Degradation Rate within water in Lower Treatment Zone, (1/day).

The next three rows contain partition coefficients.

Row 9: RKOWPZ = Oil Water Partition Coefficient in Plow Zone, (g in oil/m^3/g in water/m^3), and RKOWLZ = Oil Water Partition Coefficient in Lower Treatment Zone, (g in oil/m^3/g in water/m^3).

Row 10: RKAWPZ = Air Water Partition Coefficient in Plow Zone, (g in air/m^3/g in water/m^3), and RKAWLZ = Air Water Partition Coefficients in Lower Treatment Zone, (g in air/m^3/g in water/m^3).

Row 11: RKSWPZ = Soil Water Partition Coefficients in Plow Zone, (g in soil/m^3/g in water/m^3), and RKSWLZ = Soil Water Partition Coefficient in Lower Treatment Zone, (g in soil/m^3/g in water/m^3).

The next five rows contain oil phase characterization

```
EXAMPLE RUN FOR COMPOUND NAPHTHALENE. APPLICATION 4 TIME PER YEAR
DTZON,DPZON,DZ    1.50      .150      .300E-01
DETECT            .000
TOTAL TIME, DT    90.0      .500
TOI               .000      6.00      40.0      .000      .000      .000      .000      .000      .000      .000
DTOI              1.00      15.0      60.0      .000      .000      .000      .000      .000      .000      .000
SMLB, PHI, ROES   4.90      .435      1.40
RMUWPZ, RMUWLZ    .345      .172
RKOWPZ, RKOWLZ    .135E+04  .135E+04
RKAWPZ, RKAWLZ    .170E-01  .170E-01
RKSWPZ, RKSWLZ    .400E-02  .400E-02
WAR,CONSW,WTFO    .600E-01  .200E+04  .400
WTFW,ROEW,ROEDI   .400      .900      .800
DTAC, DTAF        366.      91.3
HO                .231E-01
RMUOPZ, RMUOLZ    .345      .173E-01
DA, VA            .000      .000
RMUAPZ, RMUALZ    .000      .000
RMUSPZ, RMUSLZ    .345      .172
ZX                .000      .150      .220      .300      .000      .000      .000      .000      .000      .000
CWZ               .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
COZ               .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
CAZ               .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
CSZ               .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
THETOX            .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
TEMP FACTOR       1.00
TEMP IN PZ       20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0
TEMP IN LZ       20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0     20.0
VWPRIME          .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02
SHC              1.00     1.00     1.00     1.00     1.00     1.00     1.00     1.00     1.00     1.00     1.00     1.00
```

Figure C2.1 Sample Input Data File

Row 12: WAR = Waste Application Rate (g waste/100g soil), CONSW = Constituent Concentration in the waste, (ppm), and WTFO = Weight Fraction of Oil in waste (kg/kg).

Row 13: WTFW = Weight Fraction of Water in waste, (kg/kg), ROEW = Density of Waste, (g/cc), and ROEOI = Density of Oil, (g/cc).

Row 14: DTAC = Application period, (days), and DTAF = Application Frequency within application period (days).

Row 15: Mo = decay rate of oil (1/day).

Row 16: RMUOPZ = Constituent Degradation Rate within Oil in plow zone, (1/day), and RMUOLZ = Constituent Degradation Rate within Oil in lower treatment zone, (1/day).

The next two rows contain unsaturated Pore Space Phase characteristics:

Row 17: DA = Dispersion Coefficient in unsaturated Pore Space (m^2/day), and VA = Advective Velocity in Unsaturated Pore Space, (m/day).

Row 18: RMUAPZ = Constituent Degration Rate within Unsaturated Pore Space in Plow Zone (1/day), and RMUALZ = Constituent Degradation Rate Within Unsaturated Pore Space in Lower Treat Zone, (1/day).

The next row contains the soil phase degradation characteristics:

Row 19: RMUSPZ = Constituent Degradation Rate within Soil in Plow Zone, (1/day), and RMUSLZ = Constituent Degradation Rate within Soil in Lower Treatment Zone (1/day),

The next six rows contain initial waste concentrations within the soil profile:

Row 20: ZX = Depths at which a new initial condition is set, (m).

Row 21: CWZ = Initial constituent concentration in water at depth ZX, (g/m^3),

Row 22: COZ = Initial concentration in Oil at depth ZX, (g/m^3),

Row 23: CAZ = Initial concentration in Air at depth ZX, (g/m^3),

Row 24: CSZ = Initial concentration in Soil at depth ZX, (g/m^3), and

Row 25: THETOZ = Initial Oil Content in Soil by Volume at depth ZX,(m^3/m^3).

The next five rows contain site environmental and soil moisture characteristics:

Row 26: Temp Factor = van't Hoff-Arrhenius Coefficient, for each month of the year,

Row 27: Temp in PZ = Temperature during each month in Plow Zone, C°, Row 28: Temp in LZ = Temperature during each month in Lower Treatment Zone, C°,

Row 29: VWPRIME = Mean daily Recharge Rate during each month, (m^3/day/m^2), and

Row 30: SHC = Saturated Water Content, during each month,(cm^3/cm^3).

Figure C2.2 shows a sample output file. The coefficient values are echoed at the beginning of the file and initial conditions are displayed. Profiles of the constituent distribution in the soil column are shown at the output times specified by the user. In addition, the output also indicates: (1) the mass remaining in the soil column, (MASS), (2) the mass that has decayed, (SDECAY), (3) the mass in the water leaving the bottom of the treatment zone, (SADW) and (4) the mass that has escaped to the atmosphere from the soil surface, (SDATOP).

Figure C2.3 shows a supplementary output file used to facilitate graphic displays of the fate of the constituent in the treatment zone. The file contains the accumulated amounts in the following categories:

MASS DECAYED = Mass of constituent lost to decay,

LEACHED WATER = Mass of constituent leaving the bottom of the treatment zone,

LEACHED OTHER = Mass of constituent lost to the atmosphere from the soil surface,

PERCENT TREATED= The percent of the applied constituent mass which does not leave the treatment zone, and

ERROR = The departure from true mass balance due to numerical errors.

```
EXAMPLE RUN FOR COMPOUND NAPHTHALENE. APPLICATION 4 TIME PER YEAR
DTZON,DPZON,DZ   1.30      .150      .300E-01
DETECT           .000
TOTAL TIME, DT   90.0      .500
TOI              .000      6.00      48.0      .000      .000      .000      .000      .000      .000      .000
DTOI             1.00      15.0      60.0      .000      .000      .000      .000      .000      .000      .000
SMLB, PHI, ROES  4.90      .435      1.40
[illegible]      .345      .172
[illegible]      [illegible] [illegible]
[illegible]      [illegible] [illegible]
[illegible]      [illegible] [illegible]
[illegible]      [illegible] [illegible] .000
[illegible]      .000      .000      .000
DTAC, DTAF       366.      91.5
HO               .231E-01
RMUOPZ, RMUOLZ   .345      .173E-01
DA, VA           .000      .000
RMUAPZ, RMUALZ   .000      .000
RMUSPZ, RMUSLZ   .345      .172
ZX               .000      .150      .220      .300      .000      .000      .000      .000      .000      .000
CWZ              .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
COZ              .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
CAZ              .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
CSZ              .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
THETOX           .000      .000      .000      .000      .000      .000      .000      .000      .000      .000
TEMP FACTOR      1.00
TEMP IN PZ      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0
TEMP IN LZ      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0      20.0
VWPRIME         .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02 .120E-02
SHC             1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00
NCOUN  INITIAL MASS G  DT =
   0  .0000       .50
DEPTH    CW           CO           CA           CS           THETAO       THETAW       THETAA
  .00  .00000       .00000       .00000       .00000       .00000       .25722       .00000
  .03  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .06  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .09  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .12  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .15  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .18  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .21  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .24  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .27  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .30  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .33  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .36  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .39  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .42  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .45  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .48  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .51  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .54  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .57  .00000       .00000       .00000       .00000       .00000       .25722       .17778
  .60  .00000       .00000       .00000       .00000       .00000       .25722       .17778
```

Figure C2.2 Sample output file.

```
  .63  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .66  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .69  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .72  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .75  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .78  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .81  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .84  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .87  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .90  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .93  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .96  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .99  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.02  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.05  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.08  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.11  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.14  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.17  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.20  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.23  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.26  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.29  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.32  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.35  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.38  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.41  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.44  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.47  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.50  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.53  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 TIME =        6.430 DT =    6.4304     MASS =   .27411E-01 VW =   .46653E-02
DECAY =  .22459     SADW =  .00000     SDATOP = .00000     ERROR =-.93132E-08 INITIA MASS = .25200
Co (g substance in oil)/(M3 control vol.)
DEPTH    CW            CD           CA           CS          THETAO       THETAW       THETAA
  .00  .00000      .00000      .00000      .00000      .00000      .25722      1.0000
  .03  .32627E-04  .15934E-04  .55466E-06  .13051E-06  .36202E-03  .25722      .17742
  .06  .32627E-04  .15934E-04  .55466E-06  .13051E-06  .36202E-03  .25722      .17742
  .09  .32627E-04  .15934E-04  .55466E-06  .13051E-06  .36202E-03  .25722      .17742
  .12  .32627E-04  .15934E-04  .55466E-06  .13051E-06  .36202E-03  .25722      .17742
  .15  .32627E-04  .15934E-04  .55466E-06  .13051E-06  .36202E-03  .25722      .17742
  .18  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .21  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .24  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .27  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .30  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .33  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .36  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .39  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .42  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .45  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .48  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .51  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .54  .00000      .00000      .00000      .00000      .00000      .25722      .17778
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Figure C2.2. Continued.

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  .57  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .60  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .63  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .66  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .69  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .72  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .75  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .78  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .81  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .84  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .87  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .90  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .93  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .96  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .99  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.02  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.05  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.08  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.11  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.14  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.17  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.20  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.23  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.26  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.29  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.32  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.35  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.38  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.41  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.44  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.47  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.50  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.53  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 TIME =       19.291 DT =    6.4304     MASS =   .32431E-03 VW =   .46653E-02
DECAY =  .25168     SADW =  .00000    SDATOP = .00000     ERROR = .64785E-07 INITIA MASS = .25200
Co (g substance in oil)/(M3 control vol.)
DEPTH     CW          CO          CA          CS          THETAD      THETAW      THETAA
  .00  .00000      .00000      .00000      .00000      .00000      .25722      1.0000
  .03  .38600E-06  .14006E-06  .65620E-08  .15440E-08  .26898E-03  .25722      .17751
  .06  .38604E-06  .14007E-06  .65626E-08  .15442E-08  .26898E-03  .25722      .17751
  .09  .38604E-06  .14007E-06  .65626E-08  .15442E-08  .26898E-03  .25722      .17751
  .12  .38604E-06  .14007E-06  .65626E-08  .15442E-08  .26898E-03  .25722      .17751
  .15  .38604E-06  .14007E-06  .65626E-08  .15442E-08  .26898E-03  .25722      .17751
  .18  .71487E-10  .00000      .12153E-11  .28595E-12  .00000      .25722      .17778
  .21  .24691E-14  .00000      .41975E-16  .98765E-17  .00000      .25722      .17778
  .24  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .27  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .30  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .33  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .36  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .39  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .42  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .45  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .48  .00000      .00000      .00000      .00000      .00000      .25722      .17778
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Figure C2.2. Continued.

```
  .51  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .54  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .57  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .60  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .63  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .66  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .69  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .72  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .75  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .78  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .81  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .84  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .87  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .90  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .93  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .96  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .99  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.02  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.05  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.08  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.11  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.14  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.17  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.20  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.23  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.26  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.29  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.32  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.35  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.38  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.41  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.44  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.47  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.50  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 1.53  .00000      .00000      .00000      .00000      .00000      .25722      .17778
 TIME =        32.152 DT =    6.4304     MASS =   .38384E-05 VW =   .46653E-02
DECAY =  .25200     SADW =  .00000     SDATOP = .00000     ERROR =-.35949E-07 INITIA MASS = .25200
Co (g substance in oil)/(M3 control vol.)
DEPTH     CW          CO          CA          CS         THETAO      THETAW      THETAA
  .00  .00000      .00000      .00000      .00000      .00000      .25722      1.0000
  .03  .45666E-08  .12311E-08  .77633E-10  .18267E-10  .19984E-03  .25722      .17758
  .06  .45675E-08  .12313E-08  .77647E-10  .18270E-10  .19984E-03  .25722      .17758
  .09  .45675E-08  .12313E-08  .77647E-10  .18270E-10  .19984E-03  .25722      .17758
  .12  .45675E-08  .12313E-08  .77647E-10  .18270E-10  .19984E-03  .25722      .17758
  .15  .45675E-08  .12313E-08  .77647E-10  .18270E-10  .19984E-03  .25722      .17758
  .18  .86209E-11  .00000      .14655E-12  .34484E-13  .00000      .25722      .17778
  .21  .10120E-14  .00000      .17204E-16  .40480E-17  .00000      .25722      .17778
  .24  .41073E-19  .00000      .69824E-21  .16429E-21  .00000      .25722      .17778
  .27  .56656E-24  .00000      .96315E-26  .22662E-26  .00000      .25722      .17778
  .30  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .33  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .36  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .39  .00000      .00000      .00000      .00000      .00000      .25722      .17778
  .42  .00000      .00000      .00000      .00000      .00000      .25722      .17778
```

Figure C2.2. Continued.

```
   .45  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .48  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .51  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .54  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .57  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .60  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .63  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .66  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .69  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .72  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .75  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .78  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .81  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .84  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .87  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .90  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .93  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .96  .00000     .00000     .00000     .00000     .00000     .25722     .17778
   .99  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.02  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.05  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.08  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.11  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.14  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.17  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.20  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.23  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.26  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.29  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.32  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.35  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.38  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.41  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.44  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.47  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.50  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  1.53  .00000     .00000     .00000     .00000     .00000     .25722     .17778
  TIME =       51.443 DT =    6.4304     MASS =   .49903E-08 VW =   .46653E-02
 DECAY =  .25200     SADW =  .00000     SDATOP = .00000     ERROR =-.14402E-06 INITIA MASS = .25200
 Co (g substance in oil)/(M3 control vol.)
 DEPTH     CW          CO          CA          CS          THETAD      THETAW      THETAA
   .00  .00000     .00000     .00000     .00000     .00000     .25722     1.0000
   .03  .58763E-11  .10145E-11  .99897E-13  .23505E-13  .12798E-03  .25722     .17765
   .06  .58782E-11  .10149E-11  .99929E-13  .23513E-13  .12798E-03  .25722     .17765
   .09  .58782E-11  .10149E-11  .99929E-13  .23513E-13  .12798E-03  .25722     .17765
   .12  .58782E-11  .10149E-11  .99929E-13  .23513E-13  .12798E-03  .25722     .17765
   .15  .58782E-11  .10149E-11  .99929E-13  .23513E-13  .12798E-03  .25722     .17765
   .18  .31279E-12  .00000     .53175E-14  .12512E-14  .00000     .25722     .17778
   .21  .79174E-16  .00000     .13460E-17  .31670E-18  .00000     .25722     .17778
   .24  .84374E-20  .00000     .14344E-21  .33750E-22  .00000     .25722     .17778
   .27  .48303E-24  .00000     .82116E-26  .19321E-26  .00000     .25722     .17778
   .30  .15642E-28  .00000     .26591E-30  .62568E-31  .00000     .25722     .17778
   .33  .27138E-33  .00000     .46134E-35  .10855E-35  .00000     .25722     .17778
   .36  .00000     .00000     .00000     .00000     .00000     .25722     .17778
```

Figure C2.2. Continued

```
 .39  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .42  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .45  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .48  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .51  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .54  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .57  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .60  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .63  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .66  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .69  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .72  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .75  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .78  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .81  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .84  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .87  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .90  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .93  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .96  .00000   .00000   .00000   .00000   .00000   .25722   .17778
 .99  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.02  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.05  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.08  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.11  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.14  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.17  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.20  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.23  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.26  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.29  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.32  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.35  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.38  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.41  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.44  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.47  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.50  .00000   .00000   .00000   .00000   .00000   .25722   .17778
1.53  .00000   .00000   .00000   .00000   .00000   .25722   .17778
```

Figure C2.2. Continued.

```
Sample OUT2 file, for plotting
   TIME      MASS DECAYED   LEACHED           LEACHED    PERCENT TREATED      ERROR
                            WATER             OTHER
    6.43      .22458944     .000000        .00000000000       100.000      -.931323E-08
   12.86      .24901854     .000000        .00000000000       100.000       .384171E-07
   19.29      .25167579     .000000        .00000000000       100.000       .647851E-07
   25.72      .25196471     .000000        .00000000000       100.000      -.366017E-07
   32.15      .25199615     .000000        .00000000000       100.000      -.359487E-07
   38.58      .25199959     .000000        .00000000000       100.000      -.292068E-07
   45.01      .25199987     .000000        .00000000000       100.000      -.103457E-06
   51.44      .25199987     .000000        .00000000000       100.000      -.144021E-06
   57.87      .25199987     .000000        .00000000000       100.000      -.148457E-06
   64.30      .25199987     .000000        .00000000000       100.000      -.148948E-06
   70.73      .25199987     .000000        .00000000000       100.000      -.149003E-06
   77.17      .25199987     .000000        .00000000000       100.000      -.149010E-06
   83.60      .25199987     .000000        .00000000000       100.000      -.149011E-06
   90.03      .25199987     .000000        .00000000000       100.000      -.149012E-06
```

Figure C2.3 Sample Supplementary Output File for Graphic Displays

C.3 FORTRAN PROGRAM DESCRIPTION

Figure C 3.1 illustrates the structure of the Enhanced RITZ model. Program section MAIN proceeds from left to right first reading the input file and then calling the subroutines from left to right. If TIME is less than TOTAL TIME the program loops back to the subroutine SLUDGE. Each program section is described below.

MAIN

The MAIN program section reads the input file, and controls the calling of the following subroutines: INTERC, OUT, SLUDGE, MONTH, DECAY, TRANS, EQUIL, OUT2, AND OUTPUT. MAIN calculates Θa, Θ_W, and water velocity using the following equations:

$$W = \Theta * \frac{(VWPRIME)^{EX}}{SHC} \qquad (C3.1)$$

where:

Θ_W = water content, $\left(\frac{m^3 water}{m^3 \text{ control volume}}\right)$,
Θ = Soil total porosity, (cm^3/cm^3),
VWPRIME($_i$) = Recharge rate during month i, $(m^3/day/m^2)$,
SCH($_i$) = Saturated water content, (cm^3/cm^3), during month i,
EX = $\frac{1}{2*SMLB+3}$,
SMLB = Soil moisture coefficient, and
i = Month since start of run.

VWPRIME and SHC are allowed to vary with time. Values are entered for each month and are used to calculate $\Delta \Theta_W$ which is used to adjust Θ_W each time step. Effective water velocity, VW, is calculated using the equation below:

$$VW = VWPRIME/\Theta_W \qquad (C3.2)$$

and is also updated each time step by a calculated Δ VW based on the calculated monthly change in VWPRIME and Θ_W. Air content is calculated by the following equation:

$$\Theta_a = \Theta - \Theta_W \qquad (\ 3.3)$$

where:

Θ_a = air content, $\left(\frac{m^3 \text{ air}}{m^3 \text{ control volume}}\right)$.

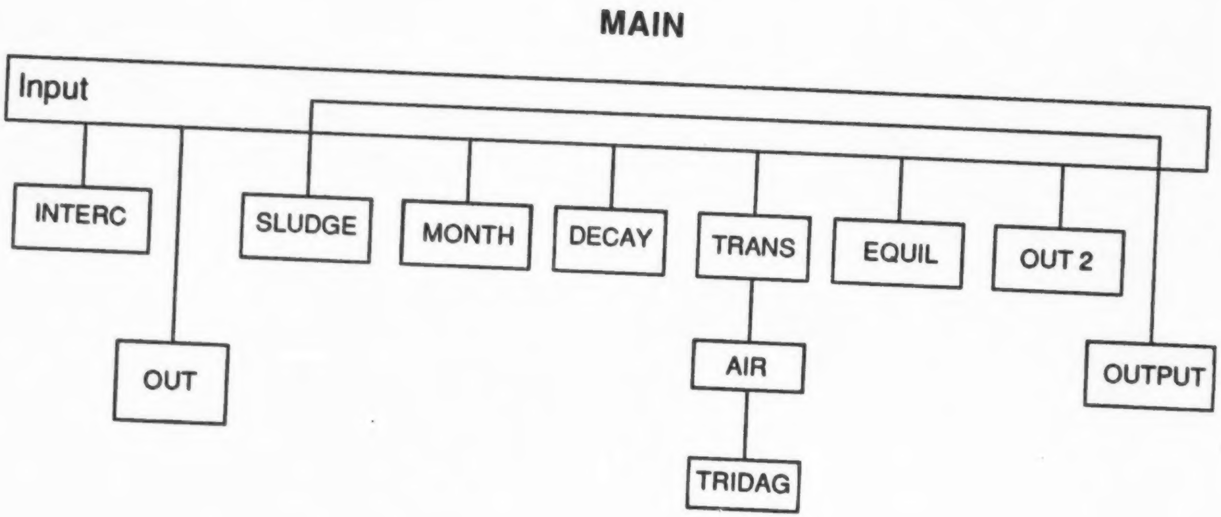
MAIN
Input
INTERC
OUT
SLUDGE
MONTH
DECAY
TRANS
AIR
TRIDAG
EQUIL
OUT 2
OUTPUT

Figure C3.1. Enhanced RITZ Model Structure.

The program will run with Θ_W equal to zero, calculating the amount decayed, leached, and lost to the atmosphere. The user should be warned that the amount lost to the atmosphere will be underestimated, since the mass of contaminant amount in the air is calculated from the mass in the water. If the water content is zero or close to zero, the amount available for transfer to the air is very small.

INPUT

Appendix C2 lists and describes the input variables read from the input file. The first line reads the title of the file. The variables are read in the order given in Appendix C2. The first 15 columns read are made up of a character field followed by up to 13 real numbers. All numbers are separated by commas.

Subroutines

INTERC

This subroutine interpolates the initial conditions, input by the user, onto the DZ grid. Concentrations are calculated at points midway between grid nodes.

OUT

This subroutine outputs initial conditions for soil air, water and soil contaminant concentration profiles along with initial Θ_o, Θ_w and Θ_a values and initial mass levels as input by the user.

SLUDGE

This subroutine adds sludge to the plow zone every DTAF days during the period DTAC each year.

MONTH

This subroutine calculates the rate of change of the time-dependent variables VW, Θw, Temp in PZ, and Temp in LZ. The rates of change between months are used in the main program to adjust these variables each time step to avoid a large jump in these variables each month.

DECAY

This subroutine carries out first order decay of the oil and the contaminant, the rate of which can vary for the contaminant with both depth and medium. The user provides decay rates for the plow zone and the lower treatment zone. Decay is calculated by the following equation:

$$C_i = C_i * \exp(-rate_{i,z} * DT) \qquad (C3.4)$$

where: C_i = concentration in medium $_i$, (g/m^3),

$\text{rate}_{(i,z)}$ = first order decay rate for concentration in medium i at depth z, (1/day), and
DT = time step (day).

TRANS

This subroutine provides advection of the contaminant in the water phase and calls the subroutine AIR. Transport in water is solved by an explicit solution algorithm. DT is calculated by the following equation:

$$DT = DZ/VW \tag{C3.5}$$

where:

DZ = depth of space element,(m).

DT is calculated by Equation C3.5 so that $\frac{VW*DT}{DZ}$ will equal 1 to minimize numerical error. The boundary condition for the water medium is:

$$C_W\ (z=o,\ t=\infty) = 0$$

where:
C_W = concentration in water, (g/m^3),
z = depth, (m), and
t = time, (days).

AIR

The subroutine AIR uses the DZ grid established by INTERC, plus two additional elements above the ground surface, in an implicit solution technique to calculate transport of the contaminant in air. Atmospheric grid elements above the soil are designated as n = 1 (upper air element) and n = 2 (air/soil interface element), making the total number of slices in the atmosphere/soil system niz + 2.

The boundry conditions assumed for the solution are as follows:

$$C_A\ (1,t+1) = 0.0$$

$$C_A\ (niz+2,\ t+1) = C_A\ (niz+1,t)$$

To allow for contaminant movement into the lower atmosphere, i.e., element n=Z, $C_A(2,t)$ is set equal to 0.0 at the beginning of each iteration. $C_A(2,t+1)$ is then calculated and represents the mass of contaminant lost to the atmosphere represented by the control volume n = 2.

TRIDAG

TRIDAG is used to solve the system of linear equations produced by the subroutine AIR. The subroutine uses a Gaussian elimination method to solve the tridiagonal matrix describing this system of equations. The method is described in detail in Carnahan et al. (1969).

EQUIL

This subroutine uses partition coefficients to calculate the contaminant concentration in each medium using the following equations:

$$MASS_S = C_S * \gamma * DZ \qquad (C3.6)$$
$$MASS_W = C_W * \theta_W * DZ \qquad (C3.7)$$
$$MASS_O = C_O * \theta_O * DZ \qquad (C3.8)$$
$$MASS_A = C_A * \theta_a * DZ \qquad (C3.9)$$

$$Total = MASS_S + MASS_W + MASS_O + MASS_A \qquad (C3.10)$$
$$C_T = \frac{TOTAL}{DZ} \qquad (C3.11)$$

$$BW = \theta_W + \theta_O\ RKOW + \theta_a *RKAW + \gamma *RKSW \qquad (C3.12)$$
$$C_W = C_{T/BW} \qquad (C3.13)$$
$$C_O = RKOW*C_W \qquad (C3.14)$$
$$C_A = RKAW*C_W \qquad (C3.15)$$
$$C_S = RKSW*C_W \qquad (C3.16)$$

where:

TOTAL = Total mass of substance in control volume, (g),
C_T = Total concentration of substance in control volume, (g/m^3),
RKOW = Oil water partition coefficient, (g in oil/m^3/g in water/m^3),
RKAW = Air water partition coefficient, (g in air/m^3/g in water/m^3), and
RKSW = Soil water partition coefficient, (g in soil/m^3/g in water/m^3).
$MASS_S$ = Mass of substance on the soil medium, (g),
C_S = Concentration of substance in soil medium, (g/m^3),
γ = Bulk soil density, (g/cm^3),
$MASS_W$ = Mass of substance in the water medium, (g)
C_W = Concentration of substance in water medium, (g/m^3),
$MASS_O$ = Mass of substance in oil medium, (g),
C_O = Concentration of substance in oil medium, (g/m^3),
θ_O = Oil content, $\left(\frac{m^3\ oil}{m^3\ control\ volume}\right)$,
$MASS_A$ = Mass of substance in air medium, (g/m^3), and
C_A = Concentration of substance in air medium, (g/m^3).

OUT2

This subroutine outputs a continuous record of totals, percent treated, and errors as indicated in Figure C2.3. The following totals are printed out: mass of constituent leached below the bottom of the treatment zone in the water, mass lost to the atmosphere, and mass of constituent decayed within the soil treatment zone. This output file (named by user) can easily be used to plot changes in the above parameters with time.

OUTPUT

This subroutine outputs concentration profiles at depth at user specified intervals. The user controls the frequency of output by variable DTO1 and the time period of output frequency DTO1 by TO1. A maximum of 10 different output frequencies can be entered.

Note to users:

The message, "Arithmetic error detected floating underflow", does not indicate the program is functioning incorrectly. This message appears whenever a concentration value is less than or equal to 10-38. Values of this magnitude are to be expected in various phases for substances which decay rapidly and/or are bound tightly to soil particles. The FORTRAN software automatically rounds this value to zero and then prints the above message.

APPENDIX D

TARGET DETECTION LIMITS IN WATER FOR CONSTITUENTS OF PETROLEUM REFINING WASTES

Table D-1 Constituents of Petroleum Refining Wastes

	Target Detection Limits in Water	
	Gangaci, 1986[a] (µg/l)	Commercial Laboratory[b] (µg/l)
1. Metals		
Antimony		
Arsenic		
Barium		
Beryllium		
Cadmium		
Chromium		
Cobalt		
Lead		
Mercury		
Nickel		
Selenium		
Vanadium		
2. Volatiles		
Benzene	10	5
Carbon disulfide	10	5
Chlorobenzene	10	5
Chloroform	10	5
1,2-Dichloroethane	10	5
1,4-Dioxane	50	100
Ethyl benzene		5
Ethylene dibromide		
Methyl ethyl ketone	10	10
Styrene		5
Toluene	10	5
Xylene		5-10
3. Semivolatile Base/Neutral Extractable Compounds		
Anthracene		5
Benzo(a)anthracene	50	5
Benzo(b)fluoranthene	50	
Benzo(k)fluoranthene		5
Benzo(a)pyrene	50	5

Table B-1 Continued

	Target Detection Limits in Water Gansecki 1986[a] (µg/l)	 Commercial Laboratory[b] (µg/l)
3. Semivolatile Base/Neutral Extractable Compounds (continued)		
Bis(2-ethylhexyl) phthalate	10	
Butyl benzyl phthalate	10	
Chrysene	10	5
Dibenz(a,h)acridine	300	5
Dibenz(a,h)anthracene	50	5
Dichlorobenzenes	10	5
Diethyl phthalate	10	20
7,12-Dimethylbenz(a)anthracene	50	
Dimethyl phthalate	10	20
Di(n)butyl phthalate		5
Di(n)octyl phthalate	10	
Fluoranthene	10	
Indene		5
Methyl chrysene		
1-Methyl naphthalene		5
Naphthalene	10	
Phenanthrene		5
Pyrene		5
Pyridine	500	5
Quinoline		10
4. Semivolatile Acid-Extractable Compounds		
Benzenethiol		10
Cresols	10	5
2,4-Dimethylphenol	10	5
2,4-Dinitrophenol	20	50
4-Nitrophenol	50	50
Phenol	25	5

[a] Data from memorandum from John H. Skinner, Director of Office of Solid Waste, U.S. EPA, December 1987.
[b] Gansecki 1986.

APPENDIX E
TARGET DETECTION LIMITS FOR SELECTED ORGANIC COMPOUNDS IN WATER

Table E.1 Target Detection Limits for Organic Compounds (Gansecki 1986)

Parameter	Units	Nominal Detection Limit
VOLATILE COMPOUNDS		
Benzene	µg/l	5
Carbon tetrachloride	µg/l	5
Chlorobenzene	µg/l	5
Chloroethane	µg/l	10
Chloroform	µg/l	5
Cyclohexane	µg/l	10
1,1-Dichloroethane	µg/l	5
1,2-Dichloroethane	µg/l	5
1,1-Dichloroethylene	µg/l	5
Ethylbenzene	µg/l	5
1,1,2,2-Tetrachloroethane	µg/l	5
Toluene	µg/l	5
1,1,1-Trichloroethane	µg/l	5
1,1,2-Trichloroethane	µg/l	5
Trichloroethylene	µg/l	5
m-Xylene	µg/l	5
o,p-Xylene	µg/l	5
BASE/NEUTRAL COMPOUNDS		
Acenaphthylene	µg/l	5
Anthracene	µg/l	5
Benzo(a)anthracene	µg/l	5
3,4-Benzofluoranthene	µg/l	5
Benzo(k)fluoranthene	µg/l	5
Benzo(g,h,i)perylene	µg/l	5
Benzo(a)pyrene	µg/l	5
Chrysene	µg/l	5
Dibenzo(a,h)anthracene	µg/l	5
Fluorene	µg/l	5
Indo(1,2,3-cd)pyrene	µg/l	5
Naphthalene	µg/l	5
Phenanthrene	µg/l	5
Pyrene	µg/l	5
Pyridine	µg/l	10

Table E.1 Continued

ACID COMPOUNDS

Parameter	Units	Nominal Detection Limit
O-Cresol	µg/l	5
m + p-Cresol	µg/l	5
Phenol	µg/l	5

OTHER DETECTABLE ORGANIC COMPOUNDS

Parameter	Units	Nominal Detection Limit
Acenaphthene	µg/l	5
Acetone	µg/l	10
Acetonitrile	µg/l	100
Acrolein	µg/l	100
Acrylonitrile	µg/l	100
Aniline	µg/l	5
Azobenzene	µg/l	5
Benz(c)acridine	µg/l	5
Benzenethiol	µg/l	10
Benzidine	µg/l	50
Benzo(j)fluoranthene	µg/l	5
Benzoic acid	µg/l	25
Benzyl alcohol	µg/l	10
Benzyl chloride	µg/l	5
Bis(2-chloroethoxy)methane	µg/l	5
Bis(2-chloroethyl)ether	µg/l	5
Bis(2-chloroisopropyl)ether	µg/l	5
Bis(chloromethyl)ether	µg/l	5
Bis(2-ethylhexyl)phthalate	µg/l	5
Bromodichloromethane	µg/l	5
Bromoform	µg/l	5
Bromomethane	µg/l	10
4-Bromophenylphenylether	µg/l	5
2-Butanone	µg/l	10
Butylbenzylphthalate	µg/l	5
Carbon disulfide	µg/l	5
4-Chloroaniline	µg/l	5
p-Chloro-m-cresol	µg/l	5
Chlorodibromomethane	µg/l	5
2-Chloroethylvinylether	µg/l	5
Chloromethane	µg/l	10
2-Chloronaphthalene	µg/l	5
2-Chlorophenol	µg/l	5
4-Chlorophenylphenylether	µg/l	5
Crotonaldehyde	µg/l	10
Dibenz(a,h)acridine	µg/l	5
Dibenz(a,j)acridine	µg/l	5
7H-Dibenzo(c,g)carbazole	µg/l	5

Table E.1 Continued

OTHER DETECTABLE ORGANIC COMPOUNDS (Cont.)

Parameter	Units	Nominal Detection Limit
Dibenzofuran	µg/l	5
Dibenzo(a,e)pyrene	µg/l	5
Dibenzo(a,h)pyrene	µg/l	5
Dibenzo(a,i)pyrene	µg/l	5
1,2-Dibromoethane	µg/l	5
Di-n-butylphthalate	µg/l	5
1,2-Dichlorobenzene	µg/l	5
1,3-Dichlorobenzene	µg/l	5
1,4-Dichlorobenzene	µg/l	5
3,3-Dichlorobenzidine	µg/l	20
Dichlorodifluoromethane	µg/l	10
1,2-cis-Dichloroethylene	µg/l	5
1,2-trans-Dichloroethylene	µg/l	5
Dichloromethane	µg/l	10
1,1-Dichloropropane	µg/l	5
1,2-Dichloropropane	µg/l	5
1,3-Dichloropropane	µg/l	5
2,2-Dichloropropane	µg/l	5
1,3-cis-Dichloropropene	µg/l	5
1,3-trans-Dichloropropene	µg/l	5
2,4-Dichlorophenol	µg/l	5
1,1-Dichloropropanol	µg/l	5
1,2-Dichloropropanol	µg/l	5
1,3-Dichloropropanol	µg/l	5
2,2-Dichloropropanol	µg/l	5
2,3-Dichloropropanol	µg/l	5
3,3-Dichloropropanol	µg/l	5
Diethylphthalate	µg/l	20
7,12-Dimethylbenz(a)anthracene	µg/l	5
2,4-Dimethylphenol	µg/l	5
Dimethylphthalate	µg/l	5
4,6-Dinitro-o-cresol	µg/l	25
2,4-Dinitrophenol	µg/l	50
2,4-Dinitrotoluene	µg/l	5
2,6-Dinitrotoluene	µg/l	5
Di-n-octylphthalate	µg/l	5
1,4-Dioxane	µg/l	100
Diphenylamine	µg/l	5
Ethyleneimine	µg/l	-
Ethylene oxide	µg/l	-
Fluoranthene	µg/l	5
Formaldehyde	µg/l	-
Hexachlorobenzene	µg/l	5
Hexachlorobutadiene	µg/l	5

Table E.1 Continued

OTHER DETECTABLE ORGANIC COMPOUNDS (Cont.)

Parameter	Units	Nominal Detection Limit
Hexachloroethane	µg/l	5
Hexachlorocyclopentadiene	µg/l	5
2-Hexanone	µg/l	10
Hydroquinone	µg/l	5
Indene	µg/l	5
Isophorone	µg/l	5
2-Methylaziridine	µg/l	-
Methylbenz(c)phenanthrene	µg/l	5
3-Methylchloanthrene	µg/l	5
Methylchrysene	µg/l	5
1-Methylnaphthalene	µg/l	5
2-Methylnaphthalene	µg/l	5
4-Methyl-2-pentanone	µg/l	10
Naphthylamine	µg/l	5
5-Nitroacenaphthene	µg/l	5
2-Nitroaniline	µg/l	5
3-Nitroaniline	µg/l	25
4-Nitroaniline	µg/l	5
Nitrobenzene	µg/l	5
2-Nitrophenol	µg/l	5
4-Nitrophenol	µg/l	10
N-Nitrosodiethylamine	µg/l	5
N-Nitrosodimethylamine	µg/l	5
N-Nitroso-di-n-propylamine	µg/l	5
Pentachlorophenol	µg/l	5
Quinoline	µg/l	5
Styrene	µg/l	5
Tetrachloroethylene	µg/l	5
1,2,3-Trichlorobenzene	µg/l	5
1,2,4-Trichlorobenzene	µg/l	5
1,3,5-Trichlorobenzene	µg/l	5
Trichlorofluoromethane	µg/l	10
2,3,4-Trichlorophenol	µg/l	5
2,3,5-Trichlorophenol	µg/l	5
2,3,6-Trichlorophenol	µg/l	5
2,4,5-Trichlorophenol	µg/l	5
2,4,6-Trichlorophenol	µg/l	5
3,4,5-Trichlorophenol	µg/l	5
Trimethylbenz(a)anthracene	µg/l	5
Vinyl acetate	µg/l	10
Vinyl chloride	µg/l	10

APPENDIX F
EXTENDED RITZ MODEL FORTRAN LISTING

```
C****************************************************************
C
C
C                     USU LTD model
C
C  Utah State University Land Treatment Demonstration model.
C
C  Programed by Craig Caupp and Dr. William Grenney
C  Civil and Environmental Engineering Departments
C  Logan, Utah 84321
C  Craig Caupp or the CEE Department make no warranties, either
C    expressed or implied with respect to this program.  In no event
C    will Craig Caupp or the CEE Department be liable for direct,
C  indirect or consequential damages resulting from the use of
C  this program.
C
C       Date of last revision May 2, 1986
C*****************************************************************

      COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                  ,JT,DZ,DT,NIZ,NDZPZ

      COMMON/PAR/VW,DW,RMUW(152),RKOW(152),RKAW(152)
     *              ,RKSW(152),RKWO(152),RKWA(152),RKWS(152)
     *              ,HO,RMUO(152),QO,DA,VA,RMUA(152)
     *              ,RMUS(152),PHI,DO,VO
      COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS

COMMON/COEFO/DEO(152),VEO(152),RMUEO(152),RKEWO(152),QEOSO(152)
     *                ,SO
      COMMON/COEFA/VEA(152),DEA(152),RMUEA(152),RKEWA(152)

COMMON/COEFW/VEW(152),DEW(152),RMUEW(152),RKEOW(152),RKEAW(152)
     *              ,RKESW(152)



C*
       CHARACTER *32 FILEI,FILEO,FILEM
       CHARACTER *80 TITLE
       CHARACTER *15 IDENT
        DIMENSION TOI(13),DTOI(13),TCHNG(13),TPZM(13),TLZM(13),ZX(13)
     +
,THETOX(13),CWZ(13),COZ(13),CAZ(13),CSZ(13),VWPRM(13)
     +            ,SHC(13)
       CHARACTER *40 ITEXT
C*
C*       Set variables used to track fate of pollutant to zero
       SDECAY=0.0
       SADW=0.0
       SDATOP=0.0
       NCOUN=0
```

```
        WRITE(1,2000)
2000        FORMAT(" ENTER FILENAME FOR INPUT DATA: ",$)
        READ(1,1000) FILEI
1000        FORMAT(A0)

C        OPEN(UNIT=1,NAME=FILEI,TYPE="OLD",READONLY)
        IF(IOREAD(7,2,0,FILEI))GOTO 999
        WRITE(1,2002)
2002        FORMAT(" ENTER FILENAME FOR OUTPUT DATA: ",$
        READ(1,1000) FILEO

C        OPEN(UNIT=8,NAME=FILEO,TYPE="NEW",CARRIAGECONTROL="LIST")
        IF(IOWRIT(8,2,0,FILEO))GOTO 996
        WRITE(1,2004)
2004        FORMAT(" ENTER FILENAME FOR PLOT OUTPUT FILE: ",$
        READ(1,1000) FILEM

C        OPEN(UNIT=9,NAME=FILEM,TYPE="NEW",CARRIAGECONTROL="LIST")
        IF(IOWRIT(9,2,0,FILEM))GOTO 997

        IF(IOWRIT(10,2,0,"ECHO.DAT"))GOTO 998



        WRITE(1,2030)
2030        FORMAT(1X,"ENTER FILE IDENTIFICATION TEXT FOR PLOT FILE
",$
        READ(1,5004)ITEXT
        WRITE(9,5005)ITEXT
5005        FORMAT(1X,A0)
5004        FORMAT(A0)

C*
        NREAD=0
5027        FORMAT(1X,I5)
        NREAD=NREAD+1
        WRITE(1,5027)NREAD

        READ(7,1001)TITLE
1001        FORMAT(A0)
        WRITE(8,2010)TITLE
        WRITE(10,2010)TITLE
2010        FORMAT(1X,A0)

        NREAD=NREAD+1
        WRITE(1,5027)NREAD
        READ(7,1002)IDENT,DTZONE,DPZONE,DZ
        WRITE(8,3002)IDENT,DTZONE,DPZONE,DZ
        WRITE(10,3002)IDENT,DTZONE,DPZONE,DZ

        NREAD=NREAD+1
        WRITE(1,5027)NREAD
```

```
      READ(7,1002)IDENT,DETECT
      WRITE(8,3002)IDENT,DETECT
      WRITE(10,3002)IDENT,DETECT
3002      FORMAT(1X,A0,11G10.3)
1002      FORMAT(A15,13F0.0)

      NREAD=NREAD+1
      WRITE(1,5027)NREAD
      READ(7,1002)IDENT,TOTALT, DT
      WRITE(8,3002)IDENT,TOTALT, DT
      WRITE(10,3002)IDENT,TOTALT, DT

      NREAD=NREAD+1
      WRITE(1,5027)NREAD
      READ(7,1002)IDENT,TOI
      WRITE(8,3002)IDENT,(TOI(I),I=1,10)
      WRITE(10,3002)IDENT,(TOI(I),I=1,10)

      NREAD=NREAD+1
      WRITE(1,5027)NREAD
      READ(7,1002)IDENT,DTOI
      WRITE(8,3002)IDENT,(DTOI(I),I=1,10)
      WRITE(10,3002)IDENT,(DTOI(I),I=1,10)
      IF(DTOI(1).GT.0.001) GOTO 2

      WRITE(10,3010)
        WRITE(8,3010)
        WRITE(1,3010)
3010        FORMAT(1X,/," **INPUT ERROR** DTOI(1) must be greater
than 0")
      IF(IOCLOS(7))GOTO 992
      IF(IOCLOS(8))GOTO 994
        STOP


      NREAD=NREAD+1
      WRITE(1,5027)NREAD
2      READ(7,1002)IDENT,SMLB,PHI,RHOSI
      WRITE(8,3002)IDENT,SMLB,PHI,RHOSI
      WRITE(10,3002)IDENT,SMLB,PHI,RHOSI

C***      INTERNAL VALUE OF RHOS, G/M3, INPUT G/CM3
C***      CONVERT G/CM3 TO G/M3
      RHOS=RHOSI*1.0E6

      NREAD=NREAD+1
      WRITE(1,5027)NREAD
      READ(7,1002)IDENT,RMUWPZ,RMUWLZ
      WRITE(8,3002)IDENT,RMUWPZ,RMUWLZ
      WRITE(10,3002)IDENT,RMUWPZ,RMUWLZ

      NREAD=NREAD+1
```

```
WRITE(1,5027)NREAD
READ(7,1002)IDENT,RKOWPZ,RKOWLZ
WRITE(8,3002)IDENT,RKOWPZ,RKOWLZ
WRITE(10,3002)IDENT,RKOWPZ,RKOWLZ

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,RKAWPZ,RKAWLZ
WRITE(8,3002)IDENT,RKAWPZ,RKAWLZ
WRITE(10,3002)IDENT,RKAWPZ,RKAWLZ

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,RKSWPZ,RKSWLZ
WRITE(8,3002)IDENT,RKSWPZ,RKSWLZ
WRITE(10,3002)IDENT,RKSWPZ,RKSWLZ

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,WAR,CONSW,WTFO
WRITE(8,3002)IDENT,WAR,CONSW,WTFO
WRITE(10,3002)IDENT,WAR,CONSW,WTFO

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,WTFW,ROEW,ROEOI
WRITE(8,3002)IDENT,WTFW,ROEW,ROEOI
WRITE(10,3002)IDENT,WTFW,ROEW,ROEOI

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,DTAC,DTAF
WRITE(8,3002)IDENT,DTAC,DTAF
WRITE(10,3002)IDENT,DTAC,DTAF

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,HO
WRITE(8,3002)IDENT,HO
WRITE(10,3002)IDENT,HO

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,RMUOPZ,RMUOLZ
WRITE(8,3002)IDENT,RMUOPZ,RMUOLZ
WRITE(10,3002)IDENT,RMUOPZ,RMUOLZ

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,DA,VA
WRITE(8,3002)IDENT,DA,VA
WRITE(10,3002)IDENT,DA,VA
```

```
NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,RMUAPZ,RMUALZ
WRITE(8,3002)IDENT,RMUAPZ,RMUALZ
WRITE(10,3002)IDENT,RMUAPZ,RMUALZ

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,RMUSPZ,RMUSLZ
WRITE(8,3002)IDENT,RMUSPZ,RMUSLZ
WRITE(10,3002)IDENT,RMUSPZ,RMUSLZ

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,ZX
WRITE(8,3002)IDENT,(ZX(I),I=1,10)
WRITE(10,3002)IDENT,(ZX(I),I=1,10)

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,CWZ
WRITE(8,3002)IDENT,(CWZ(I),I=1,10)
WRITE(10,3002)IDENT,(CWZ(I),I=1,10)

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,COZ
WRITE(8,3002)IDENT,(COZ(I),I=1,10)
WRITE(10,3002)IDENT,(COZ(I),I=1,10)

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,CAZ
WRITE(8,3002)IDENT,(CAZ(I),I=1,10)
WRITE(10,3002)IDENT,(CAZ(I),I=1,10)

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,CSZ
WRITE(8,3002)IDENT,(CSZ(I),I=1,10)
WRITE(10,3002)IDENT,(CSZ(I),I=1,10)

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,THETOX
WRITE(8,3002)IDENT,(THETOX(I),I=1,10)
WRITE(10,3002)IDENT,(THETOX(I),I=1,10)

NREAD=NREAD+1
WRITE(1,5027)NREAD
READ(7,1002)IDENT,TFACT
```

```
       WRITE(8,3002)IDENT,TFACT
       WRITE(10,3002)IDENT,TFACT

       NREAD=NREAD+1
       WRITE(1,5027)NREAD
       READ(7,1002)IDENT,(TPZM(I),I=1,12)
       WRITE(8,3006)IDENT,(TPZM(I),I=1,12)
       WRITE(10,3006)IDENT,(TPZM(I),I=1,12)
3006       FORMAT(1X,A0,12G9.3)

       NREAD=NREAD+1
       WRITE(1,5027)NREAD
       READ(7,1002)IDENT,(TLZM(I),I=1,12)
       WRITE(8,3006)IDENT,(TLZM(I),I=1,12)
       WRITE(10,3006)IDENT,(TLZM(I),I=1,12)

       NREAD=NREAD+1
       WRITE(1,5027)NREAD
       READ(7,1002)IDENT,(VWPRM(I),I=1,12)
       WRITE(8,3006)IDENT,(VWPRM(I),I=1,12)
       WRITE(10,3006)IDENT,(VWPRM(I),I=1,12)

       NREAD=NREAD+1
       WRITE(1,5027)NREAD
       READ(7,1002)IDENT,(SHC(I),I=1,12)
       WRITE(8,3006)IDENT,(SHC(I),I=1,12)
       WRITE(10,3006)IDENT,(SHC(I),I=1,12)
C*
       IF(IOCLOS(10))GOTO 998

       JT=1
       JTP1=2
       NIZ=2+DTZONE/DZ
       NDZPZ=(0.5+DPZONE/DZ)
c              volou in units of m3/m2

C*              WAR = WASTE APPLICATION RATE, G WASTE/ 100 G SOIL
C*              DPZONE = M
C*              RHOS   = G-SOIL/M3-CONTROL VOLUME
C*              WTFO   = KG-OIL/KG-WASTE
C*              ROEOI = G-OIL/CC-OIL

C* M3-OIL/M2=M*1M2*(G-SOIL/M3)*(G-WASTE/100-G-SOIL)
C*         *(KG-OIL/KG-WASTE)*(CC-OIL/G-OIL)*(1/10E6)

       VOLUO=DPZONE*RHOS*WAR*WTFO/(ROEOI*1.0E8)


C*         CMASSP = MASS OF CONSTITUENT IN PLOW ZONE
C*         RHOS    = G-SOIL/M3 CONTROL VOLUME
C*         DPZONE  = M
C*         WAR     = G-WASTE/100-G-SOIL
```

```
C*      CONSW  = CONSTITUENT IN WASTE  PPM; G-CONSTITUENT/106-G
WASTE

        CMASSP=RHOS*DPZONE*WAR*CONSW/1.0E8


C*             G0 = CONCENTRATION OF CONSTITUENT IN OIL G-C/M3-OIL
C*        G-C/M3-OIL=(G-P/M2)/(M3-OIL/M2)

        IF(VOLUO.LT.1.E-12)GOTO 37
        GO=CMASSP/(VOLUO)
37        CONTINUE

C*
        CALL INTERC(ZX,CWZ,CW,JT,DZ,NIZ)
        CALL INTERC(ZX,COZ,CO,JT,DZ,NIZ)
        CALL INTERC(ZX,CAZ,CA,JT,DZ,NIZ)
        CALL INTERC(ZX,CSZ,CS,JT,DZ,NIZ)
        CALL INTERC(ZX,THETOX,THETAO,JT,DZ,NIZ)

C*
        DO 30 IZ=1,NDZPZ+1
          RKOW(IZ)=RKOWPZ
          RKAW(IZ)=RKAWPZ
          RKSW(IZ)=RKSWPZ
          RKWO(IZ)=RKWOPZ
          RKWA(IZ)=RKWAPZ
          RKWS(IZ)=RKWSPZ
30          CONTINUE
        DO 35 IZ=NDZPZ+2,NIZ
          RKOW(IZ)=RKOWLZ
          RKAW(IZ)=RKAWLZ
          RKSW(IZ)=RKSWLZ
          RKWO(IZ)=RKWOLZ
          RKWA(IZ)=RKWALZ
          RKWS(IZ)=RKWSLZ
35          CONTINUE
C*
        TIME=0
        TIMES=0
        TIMEM=0
        TIMEO=0
        TPZ=TPZM(1)
        TLZ=TLZM(1)
        EX=1.0/(2*SMLB+3)
C******SHORT"S EQUATION
        THETAW=PHI*((VWPRM(1)/SHC(1))**EX)
        IF(THETAW.GT.0.05)GOTO 40
        VW=0
        GOTO 42
40        VW=VWPRM(1)/THETAW
```

```
42       CONTINUE
        DO 43 IZ=2,NIZ
         THETAA(IZ)=PHI-THETAW-THETAO(IZ)
43       CONTINUE
C*
C***PRINT INITIAL CONDITIONS INCLUDING INITIAL MASS
        SUMS=0.0
        DO 48 IZ=2,NIZ-1
        SCONS=CS(IZ,JT)*RHOS
        SCONW=CW(IZ,JT)*THETAW
        SCONO=CO(IZ,JT)*THETAO(IZ)
        SCONA=CA(IZ,JT)*THETAA(IZ)
        SUMS=SUMS+SCONS+SCONW+SCONO+SCONA
48       CONTINUE
C*       CONVERT CONCENTRATION TO MASS
        SUMS=SUMS*DZ
C*               RETAIN INITIAL MASS IN VARIABLE SUMI
        SUMI=SUMS

C
C        INITIALIZE OUTPUT CONTROL

        TIME=0.0
        ISTOPO=0
        IOUT=1
        TIMEO=DTOI(IOUT)


        CALL OUT (NCOUN,SUMI,JT,DETECT)

C        CALCULATE DT SO THAT VW*DT/DZ=1
        IF(VW.GT..00015)DT=DZ/VW



50       CONTINUE
        TIME=TIME+DT
        IF(TIME.GE.TIMES) CALL SLUDGE(TIME,TIMES,DTAC,DTAF,VOLUO,GO,
      +                                SUMI)

        IF(TIME.GE.TIMEM) CALL MONTH(TIME,TIMEM,DT,VWPRM,DELVW,DELTHW
      +                         ,SMLB,PHI,TPZM,TLZM,DELTPZ,DELTLZ,SHC)

        THWOT=THETAW
        THETAW=THETAW+DELTHW
        VW=VW+DELVW

C        CALCULATE DT SO THAT VW*DT/DZ=1
C        DT=2
        IF(VW.GT..00015)DT=DZ/VW
        TPZ=TPZ+DELTPZ
        TLZ=TLZ+DELTLZ
      TFPZ=TFACT**(TPZ-20)
      TFLZ=TFACT**(TLZ-20)
      DO 55 IZ=1,NDZPZ+1
        RMUW(IZ)=RMUWPZ*TFPZ
        RMUO(IZ)=RMUOPZ*TFPZ
        RMUA(IZ)=RMUAPZ*TFPZ
        RMUS(IZ)=RMUSPZ*TFPZ
55          CONTINUE
      DO 60 IZ=NDZPZ+2,NIZ
        RMUW(IZ)=RMUWLZ*TFLZ
        RMUO(IZ)=RMUOLZ*TFLZ
        RMUA(IZ)=RMUALZ*TFLZ
        RMUS(IZ)=RMUSLZ*TFLZ
60          CONTINUE


C*          EXCHANGE AND DECAY
       CALL DECAY(THWUT,SDECAY)
C


C               TRANSPORT MECHANISMS
C               ADVECTION IN WATER,
C                DIFFUSION IN AIR

       CALL TRANS (RH,SADW,SDATOP)
       NCOUN=NCOUN+1

C**********************************************************************-
****

C               EQUILIBRIUM OF SUBSTANCE BETWEEN MEDIUM
C
       BW=THETAW+THETAO(IZ)*RKOW(IZ)+THETAA(IZ)*RKAW(IZ)
     *        + RHOS*RKSW(IZ)
       IF(BW.GE..0001)CALL EQUIL (SUMS)
       IF(BW.LT..0001)WRITE(1)"WARNING BW CLOSE TO ZERO"
C**************************************************************
C        CALCULATE MASS AFTER TRANSPORT
       SUMS=0.0
       DO 49 IZ=2,NIZ-1
       SCONS=CS(IZ, JTP1)*RHOS
       SCONW=CW(IZ,JTP1)*THETAW
       SCONO=CO(IZ,JTP1)*THETAO(IZ)
       SCONA=CA(IZ,JTP1)*THETAA(IZ)
       SUMS=SUMS+SCONS+SCONW+SCONO+SCONA
49        CONTINUE
C*        CONVERT CONCENTRATION TO MASS
       SUMS=SUMS*DZ
C**********************************************************************-
****
C*                 CALCULATE ERROR
```

```
C*              SADW IS THE ACCUMULATED LEACHATE
C*              SUMS IS THE REMAINING MASS
C*              ELEMENT NIZ IS BELOW THE LOWER
C*              TREATMENT ZONE, ANY SUBSTANCE ENTERING ELEMENT NIZ
C*              IS TREATED AS LEACHATE AND IS ACCUMULATED IN
C*              SADW

C*        RMASS IS THE REMAINING MASS
      RMASS=SUMI-SDECAY-SADW-SDATOP
      ERROR=SUMS-RMASS



      CALL OUT2(TIME,SDECAY,SADW,SUMI,ERROR,NCOUN,DETECT,SDATOP)

      IF(TIME.LT.TIMEO)GOTO 80
      CALL OUTPUT(TIME,SUMS,
     *           VW,SDECAY,SADW,SDATOP,ERROR,SUMI,DETECT)

      IF(TOI(IOUT+1).LT.1.E-5)GOTO 85
      IF((TOI(IOUT).LT.TIME).AND.(TOI(IOUT+1).GT.TIME))GOTO 85
      IOUT=IOUT+1
85      CONTINUE
      TIMEO=TIMEO+DTOI(IOUT)
C*
80      CONTINUE

      JX=JT
      JT=JTP1
      JTP1=JX
      IF(TIME.LT.TOTALT)GOTO 50
      IF(IOCLOS(7))GOTO 992
      IF(IOCLOS(8))GOTO 994
      IF(IOCLOS(9))GOTO 993


      WRITE(1)"NORMAL TERMINATION"

      STOP

992        WRITE(1)"ERROR CLOSING INPUT FILE "
      IF(IOCLOS(8))GOTO 994
      IF(IOCLOS(9))GOTO 993
      STOP
994        WRITE(1)" ERROR CLOSING OUTPUT FILE"
      IF(IOCLOS(9))GOTO 993
      STOP
993        WRITE(1)" ERROR CLOSING PLOT FILE "
      STOP

996        WRITE(1)"ERROR OPENING OUTPUT FILE "
      STOP
```

```
997       WRITE(1)"ERROR OPENING PLOT FILE"
       STOP
998       WRITE(1)" ERROR OPENING ECHO FILE "
       STOP

999       WRITE(1)"ERROR OPENING INPUT FILE "
       STOP
       END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE-
EEE

C*******************************************************************
C*
C               SUBROUTINE OUT2
C       This subroutine outputs a continuous record of totals
C       for use in plotting changes over time.
C       PC:     is the percent treated, PC STARTS AT 100 AND
DECREASES
C       AS LEACHATE OCCURS.  CHANGE IN PC SHOULD DECREASE AS MATERIAL

C       DECAYS.
C********************************************************************
       SUBROUTINE OUT2(TIME,SDECAY,SADW,SUMI,ERROR,NCOUN,DETECT
     *                 ,SDATOP)
       DOUBLE PRECISION PC,XLEACH,TOTAL
       IF(NCOUN.LT.2)WRITE(9,1002)
1002       FORMAT(1X,3X,"TIME",6X,"MASS DECAYED",3X,"LEACHED",7X,
     *          "LEACHED",4X,"PERCENT TREATED",4X,"ERROR",/,1X,
     *           28X,"WATER",10X,"OTHER")
       XLEACH=SADW
       TOTAL=SUMI
       IF(TOTAL.LT.1.E-12)GOTO 70
       PC=100.*(1.-(XLEACH/TOTAL))
70       CONTINUE
       ODECAY=0.0
       IF(SDECAY.GT.DETECT)ODECAY=SDECAY
       OSADW=0.0
       IF(SADW.GT.DETECT)OSADW=SADW
       OAIR=0.0
       IF(SDATOP.GT.DETECT)OAIR=SDATOP


       WRITE(9,1000)TIME,ODECAY,OSADW,OAIR,PC,ERROR
1000
FORMAT(1X,F10.2,2X,F12.8,2X,G12.6,2X,F15.11,2X,G12.6,2X,G12.6)
       RETURN
       END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE

C*************************************************:***************
C
```

```
C
C              SUBROUTINE TRANS
C      This subroutine advects the substance in water
C      and calls the subroutine air.  Transport in water is solved
C      by an explicit solution algorithm, while transport in air
C      is solved by an implicit method.
C      The explicit method was choosen for water to reduce
C      numerical error.  The implicit method is necessary for
C      transport in air to prevent negative values and reduce
C      numerical error associated with using the explicit
C      method with small dt.
C**************************************************************
C
      SUBROUTINE TRANS (RH,SADW,SDATOP)
      COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                 ,JT,DZ,DT,NIZ,NDZPZ

      COMMON/PAR/VW,DW,RMUW(152),RKOW(152),RKAW(152)
     *             ,RKSW(152),RKWO(152),RKWA(152),RKWS(152)
     *             ,HO,RMUO(152),QO,DA,VA,RMUA(152)
     *             ,RMUS(152),PHI,DO,VO
      COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS
C*      UPPER BOUNDARY FOR WATER
      CW(1,JT)=0.0


      DO 10 IZ=2,NIZ-1
C*              CALCULATION  FOR WATER, ADVECTION ONLY
      VARW1=(DT*VW/DZ)*(CW(IZ,JT)-CW(IZ-1,JT))
      CW(IZ,JTP1)=CW(IZ,JT)-VARW1
C*              BRING CONCENTRATION ON SOIL AND OIL CURRENT
       CS(IZ,JTP1)=CS(IZ,JT)
      CO(IZ,JTP1)=CO(IZ,JT)
10       CONTINUE
C*              CALCULATE THE LEACHATE AT THE BOTTOM
C*       LEACHATE IS EQUAL TO THE PROPORTION OF SUBSTANCE
C*       MOVED FROM THE LAYER ABOVE NIZ
      VARW1=(DT*VW/DZ)*(CW(NIZ,JT)-CW(NIZ-1,JT))
      CW(NIZ,JTP1)=CW(NIZ,JT)-VARW1
      SADW=SADW+((DT*VW/DZ)*CW(NIZ-1,JT))*THETAW*DZ
C***              CALL TO SUBROUTINE TO CALCULATE TRANSPORT
C              IN AIR
      CALL AIR(SDATOP)
      RETURN
      END
C**************************************************************

C**************************************************************
C
C
C              SUBROUTINE EQUIL
C      This subroutine uses partion coefficients to calcalate
```

```
C       substance concentration in each medium.
C
      SUBROUTINE EQUIL (SUMS)


      COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *               ,JT,DZ,DT,NIZ,NDZPZ

      COMMON/PAR/VW,DW,RMUW(152),RKOW(152),RKAW(152)
     *           ,RKSW(152),RKWO(152),RKWA(152),RKWS(152)
     *           ,HO,RMUO(152),QO,DA,VA,RMUA(152)
     *           ,RMUS(152),PHI,DO,VO
      COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS
      SUMC=0.0
      SUMCA=0.0
      SUMS=0.0
      DO 10 IZ=2,NIZ-1

C               CALCULATE CT G/CONTROL VOL M3
C       M3 OF SOIL
C       (G ON SOIL/G SOIL)*(G SOIL/CONTROL VOL)
      SCONS=CS(IZ,JTP1)*RHOS
C       (G IN WATER/M3 WATER)*(M3 WATER/M3 CONTROL)
      SCONW=CW(IZ,JTP1)*THETAW
C       (G IN OIL/M3 OIL)*(M3 OIL/M3 CONTROL VOL)
      SCONO=CO(IZ,JTP1)*THETAO(IZ)
C       (G IN AIR/M3 AIR)*(M3 AIR/CONTROL)
      SCONA=CA(IZ,JTP1)*THETAA(IZ)
      CT=SCONS+SCONW+SCONO+SCONA

C       CALCULATE TOTAL CONCENTRATION IN SLICE


C       CALCULATE TOTAL MASS, NEED TO MULTIPLY BY VOLUME
C       TO GET MASS, DZ FOR UNIT M2
      SUMS=SUMS+CT*DZ

      BW=THETAW+THETAO(IZ)*RKOW(IZ)+THETAA(IZ)*RKAW(IZ)
     *        + RHOS*RKSW(IZ)


      CW(IZ,JTP1)=CT/BW
      IF(THETAO(IZ).GT.1.0E-22)CO(IZ,JTP1)=RKOW(IZ)*CW(IZ,JTP1)
      IF(THETAA(IZ).GT.1.0E-22)CA(IZ,JTP1)=RKAW(IZ)*CW(IZ,JTP1)
      CS(IZ,JTP1)=RKSW(IZ)*CW(IZ,JTP1)


C       CHECK TO SEE IF MASS BALANCE IS MAINTAINED
C       SCONS=CS(IZ,JTP1)*RHOS
C       SCONW=CW(IZ,JTP1)*THETAW
C       SCONO=CO(IZ,JTP1)*THETAO(IZ)
C       SCONA=CA(IZ,JTP1)*THETAA(IZ)
```

```
C       CT=SCONS+SCONW+SCONO+SCONA
C       SUMCA=SUMCA+CT*DZ


10        CONTINUE
        RETURN
        END

C************************************************************
C*
C*              SUBROUTINE DECAY
C*        This subroutine decays oil and calculates the new
C*        substance concentration.
        SUBROUTINE DECAY(THWUT,SDECAY)
        COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                   ,JT,DZ,DT,NIZ,NDZPZ

        COMMON/PAR/VW,DW,RMUW(152),RKOW(152),RKAW(152)
     *             ,RKSW(152),RKWO(152),RKWA(152),RKWS(152)
     *             ,HO,RMUO(152),QO,DA,VA,RMUA(152)
     *             ,RMUS(152),PHI,DO,VO
        COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS

C*           DECAY OF THE OIL MEDIUM

        EX=EXP(-HO*DT)
        DO 10 IZ=2,NIZ-1
        IF(THETAO(IZ).LT.0.00001)GOTO 10
        OMS=CO(IZ,JT)*THETAO(IZ)
        THETAO(IZ)=THETAO(IZ)*EX
        CO(IZ,JT)=OMS/THETAO(IZ)
10        CONTINUE

C*          CHANGE IN SOIL WATER CONTENT

        DO 12 IZ=2,NIZ-1
          IF((THETAW).LT.0.001)GOTO 12
            CW(IZ,JT)=CW(IZ,JT)*THWUT/THETAW
12        CONTINUE

C*          CHANGE IN SOIL AIR CONTENT

        DO 14 IZ=2,NIZ-1
          TXXX=THETAA(IZ)
          THETAA(IZ)=PHI-THETAW-THETAO(IZ)
          IF(THETAA(IZ).GT.0.0)GOTO 15
            WRITE(8,3006) IZ
3006            FORMAT(1X,/," **ERROR DECAY** Soil is saturated with
oil and"
     +              ," water at depth IZ =",I5)
            CALL CLOSE
15          IF(THETAA(IZ).LT.0.001)GOTO 14
```

```
          CA(IZ,JT)=CA(IZ,JT)*TXXX/THETAA(IZ)
14         CONTINUE

C*          DECAY WITHIN MEDIA

        DO 30 IZ=2,NIZ-1
        CWOLD=CW(IZ,JT)
          CW(IZ,JT)=CWOLD*EXP(-RMUW(IZ)*DT)
        SDECAY=SDECAY+(CWOLD-CW(IZ,JT))*THETAW*DZ
        COOLD=CO(IZ,JT)
          CO(IZ,JT)=COOLD*EXP(-RMUO(IZ)*DT)
        SDECAY=SDECAY+(COOLD-CO(IZ,JT))*THETAO(IZ)*DZ
        CAOLD=CA(IZ,JT)
          CA(IZ,JT)=CAOLD*EXP(-RMUA(IZ)*DT)
        SDECAY=SDECAY+(CAOLD-CA(IZ,JT))*THETAA(IZ)*DZ
        CSOLD=CS(IZ,JT)
          CS(IZ,JT)=CSOLD*EXP(-RMUS(IZ)*DT)
        SDECAY=SDECAY+(CSOLD-CS(IZ,JT))*RHOS*DZ
30          CONTINUE

        RETURN
        END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE


C*
C*              SUBROUTINE INTERC
C*              This subroutine interpolates the initial conditions,
C*              input by the user, onto the DZ grid.  Concentrations
C*              are calculated at points midway between grid nodes.
C*
        SUBROUTINE INTERC(ZX,CX,C,JT,DZ,NIZ)
        DIMENSION ZX(1),CX(1),C(1,1)
C*
        DO 2 I=1,NIZ
        C(I,JT)=0.0
2        CONTINUE
        IF(ZX(1).LT.1.0E-10)GOTO 1
        WRITE(8,2002)
2002        FORMAT(1X,/," ***WARNING INTERC*** Initial conditions do
not start"
    +              ," at the surface.")
C*
1        Z=-DZ/2
        C(1,JT)=0.0
        CBAS=0
        I1=0
        I2=1
        DELC=0.0
        DO 5 I=2,NIZ-1
```

```
       IF(CX(I2).LT.1E-20)GOTO 4

         Z=Z+DZ
         IF(Z.LT.ZX(I2))GOTO 10
            I1=I1+1
           I2=I2+1
           IF(ZX(I2).GT.1.0E-10)GOTO 15
C*
            ZX(I2)=10000
           DELC=0.0
           WRITE(8,2000)CX(I1)
2000           FORMAT(1X,/, " ***WARNING INTERC*** initial conditions
do not"
     +      ,/ " reach the bottom of the treatment zone.",G10.3/1X)
           GOTO 20
C*

15           IF((ZX(I2)-ZX(I1)).GT.(DZ+DZ))GOTO 30
             WRITE(8,2008)
2008             FORMAT(1X,/,1X, " **ERROR INTERC** spread in initial
condition"
     +                    ," input must be greater than 2*DZ")
             STOP
30           DELC=(CX(I2)-CX(I1))/(ZX(I2)-ZX(I1))
20           CBAS=CX(I1)
10        C(I,JT)=CBAS+DELC*(Z-ZX(I1))
5         CONTINUE
4       CONTINUE
       C(I-1,JT)=0.0
       RETURN
       END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE-
EEEEEE

C*
C*              SUBROUTINE SLUDGE
C*               Add sludge to the plow zone every DTAF days during
C*               the period DTAC each year.
C*
C*               VOLUO : VOLUME OF OIL ADDED (M3/M2 SURFACE)
C*               GO    : CONCENTRATION IN THE OIL (G/M3)
C*               TIMES : TIME TO TRIGGER NEXT APPLICATION
C*
       SUBROUTINE SLUDGE(TIME,TIMES,DTAC,DTAF,VOLUO,GO,SUMI)
C*
       COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                ,JT,DZ,DT,NIZ,NDZPZ
       COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS

C*
```

```
C*
C*          ESTABLIST THE TIME OF THE NEXT APPLICATION
C*
       IF(DTAC.GT.0.01)GOTO 5
C*       !no land application cycle
       TIMES=1.0E10

       RETURN
C*
5       IYEAR=(TIME+1.0E-6)/365
C*       !TIME TO SUSPEND FOR THIS YEAR
       SUSP=IYEAR*365+DTAC
C*       !next application this year
       TIMES=TIMES+DTAF
       IF(TIMES.LE.SUSP)GOTO 10
C*       !start again next year
         TIMES=(IYEAR+1)*365
C*
C*          CALCULATE THE AVERAGE OIL CONTENT AND CONSTITUENT
C*          CONCENTRATION IN THE PLOW ZONE
C*
C*       !no oil was added
10       IF(VOLUO.LT.1.0E-9) RETURN
C*
       SUMVO=VOLUO
       SUMMCO=VOLUO*GO
       SUMI=SUMI+SUMMCO
       DO 20 IZ=2,NDZPZ+1
         SUMVO=SUMVO+THETAO(IZ)*DZ
         SUMMCO=SUMMCO+CO(IZ,JT)*THETAO(IZ)*DZ
20          CONTINUE
       VOAVE=SUMVO/(NDZPZ*DZ)
       CMASAV=SUMMCO/(NDZPZ*DZ)
C*
       DO 30 IZ=2,NDZPZ+1
         THETAO(IZ)=VOAVE
         CO(IZ,JT)=CMASAV/THETAO(IZ)
30           CONTINUE
C*
       RETURN
       END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE

C*
C*              SUBROUTINE MONTH
C*
       SUBROUTINE MONTH(TIME,TIMEM,DT,VWPRM,DELVW,DELTHW,SMLB,PHI
     +                  ,TPZM,TLZM,DELTPZ,DELTLZ,SHC)
       DIMENSION VWPRM(1),TPZM(1),TLZM(1),SHC(1)
C*
       IYEAR=(TIMEM+1)/365
       I1=1+((TIMEM+1)-IYEAR*365)/30.416
```

```
      I2=I1+1
      IF(I2.GT.12) I2=1
      EX=1.0/(2*SMLB+3)
C       SHC IS THE SATURATED HYDRAULIC CONDUCTIVITTY SEE SHORT"S
MODEL
      THET1=PHI*((VWPRM(I1)/SHC(I1))**EX)

      THET2=PHI*((VWPRM(I2)/SHC(I2))**EX)

      DELTHW=DT*(THET2-THET1)/30.416
C*
      IF(THET1.GT.0.01) GOTO2
      VW1=0.0
      GOTO 4
2       VW1=VWPRM(I1)/THET1
4       IF(THET2.GT.0.01)GOTO 6
      VW2=0.0
      GOTO 8
6       VW2=VWPRM(I2)/THET2
8       DELVW=DT*(VW2-VW1)/30.416
C*
C*
C*               TEMPERATURE CHANGE
C*
      DELTPZ=DT*(TPZM(I2)-TPZM(I1))/30.416
      DELTLZ=DT*(TLZM(I2)-TLZM(I1))/30.416
C*
      TIMEM=TIMEM+30.416
      RETURN
      END
cEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE


C********************************************************
C
C              SUBROUTINE OUTPUT
C********************************************************
      SUBROUTINE OUTPUT(TIME,SUMS,
     *            VW,SDECAY,SADW,SDATOP,ERROR,SUMI,DETECT)
      COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                ,JT,DZ,DT,NIZ,NDZPZ
      COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS
      COMMON/OUTPUT/ TIMEOX,ITM,ISTOPO,DTOIX
      DIMENSION TOI(1),DTOI(1)


30        ISTOPO=ISTOPO+1
      IF(ISTOPO.LT.51) GOTO 31

        WRITE(8,2000)
2000        FORMAT(1X," **SUBROUTINE OUTPUT** output limited to 50
times")
```

```
      WRITE(1) "EXCEDED OUTPUT LIMIT"
        STOP

31      CONTINUE

C*           OUTPUT VALUES


35      CONTINUE

      WRITE(8,1000) TIME,DT,SUMS,VW,SDECAY,SADW,SDATOP
     *              ,ERROR,SUMI
1000      FORMAT(1X," TIME = ",F12.3," DT = ",G13.5," MASS =",G13.5,
     *   " VW =",G13.5,/,
     *   "SDECAY = ",G11.5," SADW = ",G11.5," SDATOP =",
     *    G11.5," ERROR =",G11.5," INITIA MASS =",
     *    G11.5,/,1X,"Co (g substance in oil)/(M3 control
vol.)",/,1x,
     *   "DEPTH",1X,4X,"CW"
     *   ,7X,4X,"CO",7X,4X,"CA",7X,
     *   4X,"CS",7X,3X,"THETAO",4X,3X,"THETAW",4X,3X,"THETAA")


      DO 10 IZ=1,NIZ

      COOUT=CO(IZ,JTP1)*THETAO(IZ)
      IF(COOUT.LT.DETECT)COOUT=0.0

      CWOUT=CW(IZ,JTP1)
      IF(CWOUT.LT.DETECT)CWOUT=0.0

      CAOUT=CA(IZ,JTP1)
      IF(CAOUT.LT.DETECT)CAOUT=0.0

      CSOUT=CS(IZ,JTP1)
      IF(CSOUT.LT.DETECT)CSOUT=0.0

      DEPT=(IZ-1)*DZ
      WRITE(8,1050)DEPT,CWOUT,COOUT,CAOUT,
     *              CSOUT,THETAO(IZ),THETAW,THETAA(IZ)
10      CONTINUE

1050      FORMAT(1X,F5.2,2X,4(G11.5,2X),3(G11.5,2X))


      RETURN

      END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE

C*
C*              SUBROUTINE CLOSE
```

```
C*
      SUBROUTINE CLOSE
      WRITE(1)" TERMINATED DUE TO ERROR"


      WRITE(8,3000)
3000      FORMAT(1X,/," PROGRAM TERMINATED BEFORE COMPLETION")

      IF(IOCLOS(7))GOTO 992
      IF(IOCLOS(8))GOTO 994
      IF(IOCLOS(9))GOTO 993



992      WRITE(1)"ERROR CLOSING INPUT FILE "
      IF(IOCLOS(8))GOTO 994
      IF(IOCLOS(9))GOTO 993
      STOP
994      WRITE(1)" ERROR CLOSING OUTPUT FILE"
      IF(IOCLOS(9))GOTO 993
      STOP
993      WRITE(1)" ERROR CLOSING PLOT FILE "
      STOP



      END
CEEEEEEEEEEEEEEEEEEEEEEEFEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE

C*************************************************************
C
C               SUBROUTINE OUT
C       This subroutine outputs the inital condition.
C
C*************************************************************
      SUBROUTINE OUT (NCOUN,SUMI,IOUT,DETECT)
      COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                 ,JT,DZ,DT,NIZ,NDZPZ
      COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS
      WRITE(8,2000)NCOUN,SUMI,DT
2000      FORMAT(1X,"NCOUN  INITIAL MASS G  DT =",/,1X,
     *   I5,G11.4,F5.2)
      WRITE(8,1000)
1000      FORMAT(1X,
     *     "DEPTH",1X,4X,"CW",7X,4X,"CO",7X,4X,"CA",7X,
     *   4X,"CS",7X,3X,"THETAO",4X,3X,"THETAW",4X,3X,"THETAA")
      DO 10 IZ=1,NIZ


      COOUT=CO(IZ,JTP1)*THETAO(IZ)
      IF(COOUT.LT.DETECT)COOUT=0.0
```

```
       CWOUT=CW(IZ,JTP1)
       IF(CWOUT.LT.DETECT)CWOUT=0.0

       CAOUT=CA(IZ,JTP1)
       IF(CAOUT.LT.DETECT)CAOUT=0.0

       CSOUT=CS(IZ,JTP1)
       IF(CSOUT.LT.DETECT)CSOUT=0.0

       DEPT=(IZ-1)*DZ
       WRITE(8,1050)DEPT,CWOUT,COOUT,CAOUT,
     *              CSOUT,THETAO(IZ),THETAW,THETAA(IZ)


10       CONTINUE
1050       FORMAT(1X,F5.2,2X,4(G11.5,2X),3(G11.5,2X))
12       CONTINUE
       RETURN
       END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE

C*****************************************************************
C
C
C*             SUBROUTINE AIR TRANSPORT
C
C       This subroutine uses an implicit solution technique to
calculate
C       transport of the substance in air.
C
       SUBROUTINE AIR (SDATOP)
       COMMON/VAR/CW(152,2),CO(152,2),CA(152,2),CS(152,2),JTP1
     *                 ,JT,DZ,DT,NIZ,NDZPZ

       COMMON/PAR/VW,DW,RMUW(152),RKOW(152),RKAW(152)
     *             ,RKSW(152),RKWO(152),RKWA(152),RKWS(152)
     *             ,HO,RMUO(152),QO,DA,VA,RMUA(152)
     *             ,RMUS(152),PHI,DO,VO
       COMMON/THETA/THETAO(152),THETAW,THETAA(152),RHOS
       DIMENSION A(154),B(154),C(154),D(154),T(154),tha(154)
C*       UPPER BOUNDARY FOR AIR
C*              USE THETAA(1) FOR AIR ABOVE, IT WOULD BE FOR
C*              T(2)
       THETAA(1)=1
       THETAA(niz)=thetaa(niz-1)



c*       calculate mass of material in air before transport
       xmassb=0.0
       do 50 iz=2,niz-1
       xmassb=xmassb+ca(iz,jt)*dz*thetaa(iz)
50       continue


C*              SET ARRAYS A, B, AND C


C*       ADD SLICE ABOVE SOIL SO THAT SLICE ABOVE HAS 0 FOR PREVIOUS
C*       TIME AND VALUE FOR JTP1
       M=NIZ+1
       MP1=M+1




       THA(1)=1.0
       THA(2)=1.0
       DO 80 I=3,NIZ
       THA(I)=THETAA(I-1)
80       CONTINUE
       THLAST=THETAA(NIZ-1)
       THA(NIZ)=THLAST
       THA(M)=THLAST
       THA(MP1)=THLAST

       DO 2 I=1,M

       DG=DA*((THA(IZ)**(10/3))/(PHI*PHI))
       VARA=(DT/DZ)*
     *  (((DG/THA(IZ))*(THA(IZ)-THA(IZ-1))/DZ)-VA)
       RATIO=DG*DT/(DZ*DZ)


       A(I)=-RATIO+VARA
       B(I)=1.0+2.0*RATIO-VARA
       C(I)=-RATIO
2       CONTINUE

C*              BOUNDARY AT JTP1
       T(1)=0.0
       T(MP1)=CA(NIZ,JT)
       DO 5 I=3,M
       D(I)=CA(I-1,JT)
5       CONTINUE
       D(2)=0.0+RATIO*T(1)
       D(M)=D(M)+RATIO*T(MP1)
       CALL TRIDAG (2,M,A,B,C,D,T)


       SDATOP=SDATOP+T(2)*DZ*1
C       SDABOT=SDABOT+T(M)*DZ*THA(M)
       DO 15 IZ=2,NIZ
       CA(IZ,JTP1)=T(IZ+1)
```

```
15        CONTINUE

c*        calculate mass after transport
       xmassa=0.0
       do 75 iz=2,niz-1
       xmassa=xmassa+ca(iz,jtp1)*dz*thetaa(iz)
75        continue
       XMASSA=XMASSA+T(2)*DZ*1+T(M)*DZ*THA(M)

       RETURN
       END
CEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEEE-
EEE


C              SUBROUTINE FOR SOLVING A SYSTEM OF LINEAR SIMULTANEOUS
C              EQUATIOINS HAVING A TRIDIAGONAL COEFFICIENT MATRIX.
C              THE EQUATIIONS ARE NUMBERED FROM IF THROUGH L, AND
THEIR
C              SUB-DIAGONAL, DIAGONAL, AND SUPER-DIAGONAL
COEFFICIENTS
C              ARE STORED IN THE ARRAYS A,B,AND C.  THE COMPUTED
C              SOLUTION VECTOR V(IF)..V(L) IS STORED IN THE ARRAY V.
C              TAKEN FROM APPLIED NUMERICAL METHODS; BRICE CARNAHAN
C
C
       SUBROUTINE TRIDAG (IF,L,A,B,C,D,V)
       DIMENSION A(1),B(1),C(1),D(1),V(1),BETA(154),GAMMA(154)
C
C        ....COMPUTE INTERMEDIATE ARRAYS BETA AND GAMMA...
       BETA(IF)= B(IF)
       GAMMA(IF)=D(IF)/BETA(IF)
       IFP1=IF+1
       DO 1 I=IFP1,L
       BETA(I)=B(I)-A(I)*C(I-1)/BETA(I-1)
  1       GAMMA(I)=(D(I)-A(I)*GAMMA(I-1))/BETA(I)
C
C        ....COMPUTE FINAL SOLUTION VECTOR V...
       V(L)=GAMMA(L)
       LAST=L-IF
       DO 2 K=1,LAST
       I=L-K
  2       V(I)=GAMMA(I)-C(I)*V(I+1)/BETA(I)
       RETURN
       END
```

APPENDIX G

EXAMPLE OF A MONITORING SCHEDULE FOR A FIELD PLOT DEMONSTRATION

In order to demonstrate how sampling design principles may be integrated into a field plot LTD, a hypothetical field plot sampling schedule was developed. In Table G.1 is presented an example schedule, including media to be sampled, types of analyses, and for three loading frequencies and a control plot.

At this hypothetical refinery land treatment facility operating under interim status, a reconnaissance survey has been conducted. Below treatment zone data showed significant amounts of volatile and semi-volatile organic constituents (volatile aromatic constituents present on the order of 5000 ppb; various semi-volatile naphthalenes and a few other compounds at 50-500 ppb). Analysis of the ten most prominent GC/MS peaks showed a number of nonhazardous organic constituents in all media. Metals were near background levels. Evaluation of groundwater data also indicated possible contamination from the land treatment area.

After evaluating reconnaissance data, the regulatory agency determined that a field scale plot study was appropriate. Laboratory studies suggested that a lower range of waste loads than previously used may be appropriate at the site (Loading Rate A). Past practices involved a one-time annual application of wastes. The field plot study will utilize a one-time waste load application at two rates (A and B) as well as a two-time-per-year application rate of the lower loading rate A.

Table G.2 shows the proposed schedule for waste application and monitoring. An additional control plot was selected on the ISS site to evaluate the apparent rate of degradation of previously applied waste.

Three plots were located and constructed on nearby untreated soils similar to those in the ISS area. These plots will receive waste loading rate A at one time per year, waste loading rate B at one time per year, and waste loadin rate A twice per year. Because the groundwater is extremely shallow and soils of high permeability exist at the site, a monitoring well was located immediately downgradient of each field plot. The annual average precipitation is 45 inches, suggested that soil-moisture sampling will be feasible. Existing groundwater wells will be monitored at six-month intervals in order to evaluate any changes in hazardous constituent concentrations.

Background sampling was conducted at two soil sites in the area of the proposed field plots and showed no Type III organic compounds above detection limits at any soil depth. Type I and III analyses were performed for four samples of each applied waste. In the case of the two-time application, two samples were evaluated at each application after careful compositing. Groundwater monitoring results were available for the ISS monitoring sites. A one-time sampling of the field plot wells showed no detectable Type III constituents. Metal concentrations were assumed to be similar to Part 265 upgradient wells.

The Type II analysis chosen for evaluating specific hazardous constituents was SW-846 Method 8020 (U.S. EPA 1982b) for volatile aromatic hydrocarbons, since these were in the highest concentrations in the ISS soil zones and below the treatment zone, and are expected to be the most mobile compounds. Other hazardous constituents will be more infrequently monitored with Type III analysis. It was not felt necessary to do further evaluation of metals. Toxicity studies using two bioassays will be conducted at the same frequency as the Type II analysis.

Zone of incorporation sampling is scheduled in order to evaluate a presumed first-order kinetic rate degradation (i.e., a higher proportion of sampling closest to the time of waste application). It was determined from a small-scale study that 5 Type II samples would be required at each sampling time. Waste would be pre-mixed with ZOI soils in a pug mill to reduce variablilty of waste distribution in the ZOI. Five or 6 ZOI samples over time are expected to be sufficient to establish degradation rates. Oil degradation will also be measured with Type I analysis.

Type III core samples (ZOI to BTZ) will be taken at six month intervals from the first application. Three replicate samples within each treatment plot will be analyzed for Type III compounds and metals at each depth.

Soil-pore liquid monitoring was established on a schedule similar to the ZOI sampling. Soil mobility calculations based on the land treatment model indicated that movement out of the treatment zone could occur within one to three months. Two soil-pore liquid samplers were located in each treatment plot. An effort will be made to time soil-pore liquid sampling events within the general schedule shown, following significant precipitation events.

The need for further analyses will be reviewed at the end of the year period. Issues to be evaluated are whether or not high concentrations of the Appendix VIII compounds would be found in the BTZ soil and whether or not significant leaching could be identified.

Evaluation of results may determine that PHCs or other compounds have not degraded. There may be a need to establish a consistent sampling schedule beyond the first year shown in the example schedule.

First-year results may also indicate some compound movement based on results of intermediate soil zone sampling. More intensive sampling in these zones may be needed. In general, it is not possible to recommend a defined schedule for follow-up studies. Evaluation of results should be conducted during the performance of the LTD to allow modification of the monitoring schedule.

Table G.1 Example of a Monitoring Schedule for a Field Plot Study

Plot	Waste Application Frequency	Sampling Schedule (Day from initial application)									
		0	30	60	120	180	210	240	270	300	360
Control	0	Z1,2		Z1,2	Z1,2	Z1,2,3 SP3			Z1,2		Z1,2 C3,SP3,G3
WL(A)	1/yr	Z1,2 SP3	Z1,2 SP2	Z1,2 SP2	Z1,2	Z1,2 SP3,C3			Z1,2		Z1,2 SP3,C3,G3
WL(B)	1/yr	Z1,2 SP3	Z1,2 SP2	Z1,2 SP2	Z1,2	Z1,2 SP3,C3		Z1,2			Z1,2 SP3,C3,G3
WL(A)	2/yr	Z1,2 SP3	Z1,2	Z1,2 SP2	Z1,2	Z1,2 SP3,C3	Z1,2	Z1,2 SP2		Z1,2	Z1,2 SP3,C3,G3

Definition of Terms

Sample: Z- zone of incorporation; C- soil core samples from ZOI to BTZ; SP- soil-pore liquid; G-groundwater

Type of Analysis: 1- Type I; 2- Type II; 3- Type III

Waste Loading and Frequency: WL(A)- waste loading rate A; WL(B)- waste loading rate B; two frequencies-1/yr and 2/yr